Sunday Afternoon, November 14, 2004

Biomaterials Plenary Session
Room 210D - Session BP-SuA

Biomaterials Plenary

Moderator: A. Chilkoti, Duke University

3:00pm **BP-SuA1 The Biobarcode Approach to Detecting DNA, Proteins, and Small Molecules*, C.A. Mirkin,*** Northwestern University **INVITED**

A great deal of effort has been devoted to evaluating the potential of nanostructures in biodiagnostic applications for human disease detection and biowarfare and terrorism defense. These technologies compete with many of the industry standards based upon fluorescence, radioactivity, and PCR. This presentation will explore the advantages and disadvantages of nanostructures in biodiagnostics and attempt to put recent advances in the context of this competitive field.

3:40pm **BP-SuA3 Biological Surface Science: Quo Vadis?*, M. Grunze,*** University of Heidelberg, Germany **INVITED**

Michael Grunze, Institute for Molecular Biophysics, University of Maine, and Lehrstuhl für Angewandte Physikalische Chemie, Universität Heidelberg, Germany Both the elemental and molecular structure sensitivity of established surface spectroscopic techniques are of great value in the development and failure analysis of biomedical devices. However, analysis is –by necessity- done ex situ, so the question always remains if the conclusions derived from the data are representative of the system in a physiological environment. Significant technical complications in carrying out the experiments and in data interpretation are encountered when spectroscopy is done in situ, for example in Vibrational Sum Frequency Generation, Infrared Microscopy, or X-ray absorption- and emission spectroscopy using synchrotron radiation. In general, the problem turns out to be far more complicated than anticipated by any physical scientist. If at all, only simplified model systems of biomedical relevance are presently amenable to in situ surface spectroscopy experiments. However, their detailed analysis, combined with the knowledge derived from biological and medical experiments, can in some cases lead to a better understanding of biomedical processes. This talk will discuss both success and failures; I will discuss examples of failure analysis and failure (limitations) of the application of biological surface science in experimental systems. Examples will also be presented that will demonstrate the significant contributions of Biological Interface Science in providing new insights into biological and biomedical problems.

4:20pm **BP-SuA5 Single Molecule Force Spectroscopy: Mechanics of Bio-Molecules and their Interactions*, H. Gaub,*** University of Munich, Germany **INVITED**

Local interactions between bio-molecules regulate the complex diversity of life. With the development of AFM-based techniques, which allow control and measurement of interaction forces between individual molecules at physiological conditions, a multitude of essential processes such as molecular recognition and protein folding have become accessible at unparalleled resolution and sensitivity. Moreover, the description of molecular devices and machines based on forces rather than thermodynamic variables has provided novel insight into their biological function. This lecture will highlight the advances of the recent years.

Applied Surface Science
Room 210A - Session AS-MoM

SIMS I - Cluster Probe Beams and General Topics

Moderator: I. Gilmore, National Physical Laboratory, UK

8:20am **AS-MoM1 Application of TOF-SIMS to Environmentally Relevant Surface and Interfaces***, **D.J. Gaspar**, A. Laskin,* Pacific Northwest National Laboratory*; B.J. Finlayson-Pitts,* University of California, Irvine*; B.M. Sass,* Battelle Memorial Institute

TOF-SIMS analysis is an invaluable tool for analysis of environmentally relevant samples. The molecular identity and distribution of surface species can be essential in understanding environmental samples. In the Environmental and Molecular Sciences Laboratory, we have applied TOF-SIMS analysis to problems in atmospheric and environmental chemistry. Some examples presented here include: identification and measurement of fatty acids on aerosol particles, measurement of extent of reaction between NaCl and hydroxyl radicals,@footnote 1@@super ,@ @footnote 2@ investigation of the interaction between glass and gaseous nitric acid,@footnote 3@ and determination of heavy metal distributions in weathered, pressure-treated wood. In the first example, fatty acids were identified on field collected atmospheric aerosols as a function of time. Next, hydroxyl radicals were found to reacted with NaCl particles in the laboratory to produce basic species, while in the third example, the reaction products of gaseous nitric acid and borosilicate glass were determined to segregate on the glass surface in precipitates according to solubility. Finally, the distribution of copper, chromium and arsenic, as well as other metals, were measured in pressure treated wood after extended weathering. Each of these examples demonstrates the utility of TOF-SIMS in identifying species and determining distributions on environmentally relevant surfaces. @FootnoteText@ @footnote 1@ D.J. Gaspar, A. Laskin, W. Wang, S.W. Hunt, and B.J. Finlayson-Pitts. Applied Surface Science, in press, 2004.@footnote 2@ A. Laskin, D.J. Gaspar, W.H. Wang, S.W. Hunt, J.P. Cowin, S.D. Colson, B.J. Finlayson-Pitts. Science, 301 (2003) 340-344,"@footnote 3@ Y. Dubowski, A. L. Sumner, E. J. Menke, D. J. Gaspar, J. T. Newberg, R. C. Hoffman, R. M. Penner, J. C. Hemminger and B. J. Finlayson-Pitts. Physical Chemistry Chemical Physics, in press, 2004.

8:40am **AS-MoM2 Cluster Primary Ion Beam Secondary Ion Mass Spectrometry for 2 and 3 Dimensional SIMS Analysis***, **G. Gillen**, P. Chi, A.J. Fahey, C.M. Mahoney, M.S. Wagner,* National Institute of Standards and Technology **INVITED**

The use of novel monoatomic and cluster primary ion beams for Secondary Ion Mass Spectrometry (SIMS) has several potential advantages for surface analysis. Cluster ion sputtering results in a reduced penetration depth for the constituent atoms of the cluster, which should improve SIMS depth resolution and minimizes the sputter depth over which the build up of the primary beam gives non-linear sputter and ion yield enhancements (the so-called transient region). Cluster bombardment may also reduce sputter-induced topography created during ion beam analysis of metal films. For organic surface characterization, cluster primary ion beam offers large improvements in sensitivity and, in selected cases, immunity to primary-beam-induced degradation of the sample. At NIST we are working on the application of novel primary ion beam SIMS for practical surface analysis. Several types of prototype ion sources are currently being evaluated for this application including; SF5+ , C8- and C60+. A variety of materials have been analyzed using these new ion sources including low energy ion implants of arsenic and phosphorous in silicon, boron delta-doped layers, surface metals, metal films, organic films and polymers. Recent key findings include the observation of improved depth resolution for semiconductor analysis and a reduction in beam-induced topography for metal films. Our most recent efforts have been focused on extending the cluster SIMS technique for the molecular depth profiling of organic thin films. Combined with secondary ion imaging we will demonstrate the unique capability of cluster SIMS to provide true 3 dimensional molecular surface analysis.

9:20am **AS-MoM4 Fundamentals and Applications of a New Bi-cluster Liquid Metal Ion Source***, **F. Kollmer**, P. Hoerster, R. Moellers, D. Rading, T. Grehl, E. Niehuis,* ION-TOF GmbH, Germany

In recent years Au cluster primary ions emitted from a LMIS (liquid metal ion source) have been successfully applied for the analysis of organic surfaces by TOF-SIMS. Compared to monoatomic primary ion bombardment the use of Au clusters leads to a considerable enhancement of the secondary ion yield up to several orders of magnitude. As the corresponding increase in the damage cross section is much smaller, the ion formation efficiency as a cumulative measure of the sensitivity of the analysis process, also increases significantly. In particular the Au cluster source combines the fundamental benefits of cluster ion bombardment with a high brightness source allowing to push the lateral resolution in organic imaging down to the 100-nm range. In this contribution fundamental as well as practical aspects of a newly developed Bi-cluster liquid metal ion source are addressed and compared with the capabilities of a Au cluster source. The Bi-cluster source offers excellent prospects for organic surface analysis since a large fraction of the primary ion current is emitted as singly and doubly charged clusters (up to Bi@sub 7@@super 2+@). Even at low emission currents stable operation is achieved which is advantageous with respect to the lifetime of the source and the spot size of the primary ion beam.

9:40am **AS-MoM5 TOF-SIMS Studies using a Newly Developed C@sub 60@@super +@ Primary Ion Gun: Fundamental Aspects and Applications***, **R. Moellers**, F. Kollmer, D. Rading, T. Grehl, E. Niehuis,* ION-TOF GmbH, Germany

Recently it was shown that cluster primary ion bombardment leads to a considerable enhancement of the secondary ion emission efficiency for organic materials. This enhancement not only increases the sensitivity for molecular species up to several orders of magnitude, but also pushes the useful lateral resolution in organic imaging down to the sub-µm range. C@sub 60@ is currently discussed to be the most efficient projectile for organic surface analysis and first results have been published announcing depth profiling capabilities of C@sub 60@@super +@ primary ions on organic materials. We have integrated a newly developed C@sub 60@ ion gun into the TOF.SIMS 5. The gun can be operated both as sputter gun and as analysis gun with a primary ion energy of up to 20 keV using doubly charged C@sub 60@ particles. The new setup allows the direct comparison between different primary ions such as C@sub 60@@super +@, Au@sub 1@@super +@, Au@sub 3@@super +@ as well as the combination of metal cluster ions and C@sub 60@ in dual beam depth profiling. C@sub 60@@super +@ primary ions were used to extend our systematic investigation on the influence of different primary ion species, including metal cluster ions as well as monoatomic primary ions, on secondary ion parameters such as yield Y, damage cross section @sigma@ and efficiency E = Y/@sigma@. Those parameters have been evaluated for a variety of different sample materials and sample preparations allowing a classification of the merits of C@sub 60@ in different fields of application. Beside these fundamental aspects of cluster ion beam bombardment, the use of C@sub 60@@super +@ beyond the static limit on different samples will be highlighted.

10:00am **AS-MoM6 ToF-SIMS Quantitation of PDMS at the Surface of a Dehydrated Commercial Hydrogel Material***, **J.A. Gardella, Jr.**,* State University of New York at Buffalo

The method of standard additions was performed in order to determine the amount of PDMS present at the surface of a dehydrated hydrogel material. Known amounts of a PDMS monomer were added to the surface and allowed to equilibrate. Peak ratios of 73Da (C3H9Si+):69Da(C4H5O+) and 147Da(C5H15Si2O+):113Da(C6H9O2+) were plotted against ng of PDMS added to the surface. A linear fit was applied to the data and the amount of PDMS present at the native surface was determined.

10:20am **AS-MoM7 SIMS Trace Uranium Measurements in HfO Films with the ims-1270***, **A.J. Fahey**,* National Institute of Standards and Technology

The presence of radioactive elements, such as U, even at trace levels can make it impractical or impossible to use some materials in semiconductor applications because of randomly induced logic-errors from the decay of the radioactive element. Efforts have been put forth to determine the trace concentration of uranium in a HfO film deposited on Si. This measurement is complicated by the fact that high mass resolution is needed to resolve @super 178@HfSiO@sub 2@ from @super 238@U. In addition, high sensitivity is required in order to measure trace quantities of uranium in the film. The ims-1270 at the National Institute of Standards and Technology has been used for this purpose. Large magnetic sector SIMS instruments are not generally used by the semiconductor SIMS community because of their size and cost. However, they can address some very specific problems that cannot be addressed by smaller instruments that do not have the mass resolution or the transmission. A mass resolution of ~5000 is easily achieved with the ims-1270, while maintaining nearly full transmission. This condition can be used to separate the interference at U. An apparent concentration of U between ~1-10 ppm was measured is the available films. The measurement method, the data and attempted quantification of the measured concentration will be discussed.

10:40am **AS-MoM8 Improved Analysis of Bulk Insulators using Magnetic Sector SIMS with O@sub 2@@super +@ Primary Beam and Electron Beam Adjacent to Analysis Area***, F.A. Stevie, C. Gu, A. Pivovarov, R. Garcia, D.P. Griffis,* North Carolina State University

The application of a new method(1) for magnetic sector SIMS analysis of thick film and bulk insulators using O@sub 2@@super +@ primary beam with electron beam adjacent to the area of interest has been extended. Excellent results have been obtained for a wide range of bulk insulators, including SiO@sub2@, LiNbO@sub 3@, Al@sub 2@O@sub3@, AlN, and a low-K dielectric. Quantification of impurities in bulk insulators has also been demonstrated as evidenced by depth profiles of B implanted in silica, Ti in LiNbO@sub 3@, and Be in Al@sub 2@O@sub 3@. The 1E15 atoms/cm@super 3@ detection limit obtained for the Be in Al@sub 2@O@sub 3@ cannot be achieved using quadrupole analyzers because of the inability to filter the Al@super 3+@ mass interference. Profiles several micrometers deep have been routinely achieved. Accurate concentrations for several elements have also been obtained on NIST standard glasses. The analysis of the low-k dielectric was significant because direct electron bombardment results in decomposition of this material. While the efficacy of this method is indisputable, the apparently self compensating mechanism is not understood. It is clear that a conductive coating encompassing the sputtered area is required and that the electron beam must impact within approximately 100@micron@m of the analyzed area. While it is not clear which if any of these charge compensation mechanisms predominate, the most probable mechanisms contributing to positive charge compensation include secondary and/or backscattered electrons and electron beam induced conductivity (EBIC). Efforts to understand the charge neutralization mechanism for this method continue. (1) A. L. Pivovarov, F. A. Stevie, D. P. Griffis, Appl. Surf. Sci. (2004) in press

11:00am **AS-MoM9 Ionization of Al Atoms Emitted from Al Metal***, **X. Chen**,* University of California, Riverside*; Z. Sroubek,* Czech Academy of Sciences, Czech Republic*; J. Yarmoff,* University of California, Riverside

Ion-surface charge exchange is a central process in many surface analysis techniques, such as ion scattering spectroscopy (ISS), secondary ion mass spectrometry (SIMS) and electron stimulated desorption (ESD). Recently, we achieved a better understanding of homogeneous charge exchange between metal ions and metal surfaces, which gives a general insight for all the above techniques and is especially critical in analysis of SIMS data. Atomically clean and modified Al (100) surfaces in ultra-high vacuum were bombarded by 2 and 5 keV Xe@super +@ ions. The absolute ionization probability of energetic (> 500 eV) recoiled particles was measured with time-of-flight, and then used to calibrate the energy and angular distributions of low energy (10-600 eV) sputtered ions collected with an electrostatic analyzer. The independent particle model of non-adiabatic surface-atom charge-exchange, which has typically been used to analyze single scattering events, is shown to accurately describe all of the experimental data from a few eV (typical sputtering energy) to the keV (typical scattering and recoiling energy) range. Extensions of this work to other clean metal surfaces, such as Fe, which has a d-band, will be discussed. Also, we plan to perform homogeneous scattering experiments with a novel liquid metal ion source (LMIS), to determine absolute homogeneous ionization probabilities for well-defined trajectories.

Biomaterial Interfaces
Room 210D - Session BI-MoM
In-Situ Spectroscopy of Biomolecules at Interface

Moderator: M. Grunze, University of Heidelberg, Germany

8:20am **BI-MoM1 High-Resolution Structural and Dynamic Characterization of Proteins on Biomaterial Surfaces***, **P.S. Stayton**, G.P. Drobny,* University of Washington **INVITED**

The development of materials with bioactive interfaces is a major focus of the biomaterials and tissue engineering communities. There is also considerable interest in the immobilization of active peptides and proteins in separations, diagnostics, proteomics, and cell culture technologies. In order to design appropriate biomaterial modification strategies where activity is retained, it is desirable to elucidate how protein structure, dynamics and orientation are related to the biomaterial surface properties and immobilization chemistries. Solid-state NMR techniques provide an opportunity to determine these molecular structure and dynamics properties of proteins and peptides on many different types of biomaterial surfaces. In particular, the high-resolution backbone conformation of proteins can be determined, the binding "footprint" - or which amino acid side-chains actually contact the surface can be determined, the role of water at the protein-material interface can be investigated, the dynamics of specific protein side-chains can be determined, and the orientation of the protein on the crystal surface can be determined. Homonuclear and heteronuclear dipolar recoupling solid-state NMR techniques, combined with dynamic studies, have been applied to determine the structure, dynamics and orientation of proteins and peptides immobilized on polymeric biomaterial surfaces, surface-modified nanoparticles, and on inorganic crystals such as hydroxyapatite.

9:00am **BI-MoM3 Protein-Surface Interactions Studied with Internal Reflection Ellipsometry***, **H. Arwin**, M. Poksinski,* Linköping University, Sweden

Spectroscopic ellipsometry (SE) used in internal reflection mode exhibits very large sensitivity for in situ protein adsorption on thin metal layers if used at surface plasmon (SP) resonance conditions@footnote 1@. Compared to external SE, the protein layer induced changes in the ellipsometric parameter @DELTA@ are several orders of magnitude larger. Using this high sensitivity it becomes possible to extract more details than only protein surface mass density (or film thickness) from SE data. In situ determination of the microstructure of adsorbed protein layers, e. g. in terms of mass distribution perpendicular to a surface, is within reach. Another implication is an increased sensitivity in biosensor applications. The enhanced sensitivity is here verified experimentally with adsorption studies of human serum albumin on gold and the possibility to model protein layer microstructure from SE data is demonstrated. Access to such detailed information is of relevance to understand conformation, surface interaction, dynamics and function of proteins at interfaces. The increased sensitivity is discussed in a thin film approximation of the complex reflectance ratio. It is found that the @DELTA@-sensitivity is inversely proportional to the difference between the damping @GAMMA@ of an SP if the metal is semi-infinite and the change in damping due to that the metal film is thin. The SE sensitivity is thus in principle unlimited as the metal-film induced change in damping can be selected with the film thickness and made to match @GAMMA@. However, the sensitivity becomes finite due to non-idealities of the sample, beam divergence, finite bandwidth of the light, etc. @FootnoteText@ 1. H Arwin, M Poksinski and K Johansen, Total internal reflection ellipsometry: principles and applications, Appl Opt, in press; M Poksinski and H Arwin, Protein monolayers monitored by internal reflection ellipsometry, Thin Solid Films 455-456 (2004) 716-721.

9:20am **BI-MoM4 Angle-resolved Imaging Surface Plasmon Resonance***, D.A. Armitage,* The University of Nottingham, UK*; **P.M. Williams**,* The University of Nottingham, UK, U.K.

Surface plasmon resonance (SPR) has evolved in recent years into a commercially recognized technique for analyzing surface interactions with a film thickness resolution on the sub-nanometer scale. SPR imaging can also be employed to obtain data on the spatial distribution of molecules at surfaces. However, the instrumentation currently used in SPR imaging experiments has reduced capabilities for precise SPR angle and hence thickness and refractive index measurements compared to conventional non-imaging systems. By combining a non-imaging SPR system with a micro-positioning stage we demonstrate that a 2-D image of SPR response can be produced whilst retaining high precision angle sensitivity.

9:40am **BI-MoM5 Feasibility Study of a Waveguide Excitation Fluorescence Microscope for Micro and Nanoscale Characterization of Bio-Interfaces***, **H.M. Grandin**, B. Städler, J. Vörös, M. Textor,* Swiss Federal Institute of Technology (ETH), Switzerland

The ability to investigate the interactions that occur between a biological system and a surface, be it a native biological surface or a synthetic surface, is of critical importance to our fundamental understanding of biomaterials and their many applications in biosensors, medical implants, and tissue engineering. Our development of a Waveguide Excitation Fluorescence Microscope (WExFM) satisfies this need uniquely by providing a means for the quantitative study of bio-interfacial interactions in-situ, e.g.: protein adsorption and cell adhesion, with both temporal and spatial resolution. Although other techniques are capable of either quantitative studies, e.g.: optical waveguide lightmode spectroscopy, or of spatially resolved imaging at the interface, e.g.: total internal reflection fluorescence microscopy, the WExFM is the only technique currently available which can provide both simultaneously. Further advantages include high target sensitivity for fluorescence detection (femtoMolar range) and high surface specificity (ca. 100 nm perpendicular to the waveguide), as well as, the capability to perform multicolour imaging, large area analysis with submicron resolution, and 'built-in' calibration of fluorescent light gain. Preliminary results from streptavidin-biotin binding studies have been obtained with sub-picoMolar sensitivity, thus, demonstrating the feasibility of this technique. In this presentation the principles and experimental set-up of the WExFM will be introduced, potential applications for in-situ, real-time quantitative monitoring of protein- and cell-surface interactions will be discussed and finally, first results demonstrating the feasibility of the WExFM will be presented.

10:00am **BI-MoM6 In situ Sum Frequency Generation Characterization of Peptide Monolayers on Hydrophobic and Charged Surfaces***, **N.T. Samuel,*** University of Washington*; K. McCrea,* The Polymer Technology Group*; L.J. Gamble,* University of Washington*; R.S. Ward,* The Polymer Technology Group*; P.S. Stayton,* University of Washington*; G.A. Somorjai,* University of California at Berkeley*; D.G. Castner,* University of Washington

Immobilization of bioactive peptides is an active research area for diagnostics, cell culture and biomedical implants. Previous studies have shown well-defined sequences of lysine (K) and leucine (L) containing peptides spontaneously adsorb onto hydrophobic substrates with either @alpha@-helix or @beta@-sheet secondary structures. In this study the adsorption of these peptides onto hydrophobic and charged surfaces has been characterized in situ with IR-Visible Sum Frequency Generation (SFG) spectroscopy. The SFG spectra in the CH, NH and OH stretch regions show the adsorption of the LK peptides onto these substrates is mediated by interactions through their leucine (hydrophobic surfaces) and lysine (charged surfaces) residues. These hydrophobic and electrostatic interactions are accompanied by ordering of the functional groups involved in the interaction. Ordering of water molecules at these interfaces is also observed. SFG spectra in the amide I region were used to examine the secondary structure of the LK peptides. For the @alpha@-helix LK peptide the @alpha@-helix secondary structure is maintained upon dehydration of the sample, even though significant changes in the side chain ordering was observed. Polarization-dependent Near-edge X-ray Absorption Fine Structure (NEXAFS) experiments were also done on the adsorbed peptides. The results demonstrate that the N1s->@pi@*@sub CONH@ feature in the Nitrogen K-edge is sensitive to the secondary structure of the adsorbed peptide. NEXAFS experiments also confirm the highly ordered nature of the adsorbed peptides.

10:20am **BI-MoM7 Measurement of Conformational Changes of Surface Bound Biomolecules: a Novel Strategy for Analytical Biosensing***, **D.A. Russell**, L.M. May,* University of East Anglia, UK

A large number of biomolecules change conformation upon interaction with specific substrates. Whilst spectroscopic techniques (such as CD, NMR and IR) provide sensitive measurement of secondary structure in solution, they are not amenable for the development of surface bound sensing technologies based on analyte induced conformational changes. Surface plasmon resonance (SPR) is a surface sensitive technique capable of measuring changes in refractive index (RI) that occur in proximity to the sensor interface. By depositing biomolecules onto the gold-coated sensor surface of an SPR instrument it is possible to measure changes of secondary structural conformation as a function of substrate concentration. A number of biomolecules including, polypeptides, proteins and enzymes, have been formulated as SAMs on SPR sensor surfaces and varying concentrations of substrates or mild denaturants have been passed over the monolayer surface to elicit secondary structural changes. For example, a dramatic increase in the SPR signal (m°) was observed when polylysine was induced into the alpha-helical conformation with ethanol. Similarly, the SPR signal was related to other secondary structures (including beta-sheet and random configurations) of both polypeptides and the protein Concanavalin A. The intensity of the SPR signal being related to the RI of the secondary structural configuration of the biomolecule. Development of this sensing strategy has focused on the self-assembly of urease in order to measure the conformational change of this enzyme as a function of heavy metals. On the sensor surface, the SPR signal from the urease monolayer linearly increased in intensity as a function of cadmium concentration in the range 0 - 10 mg/L. These data show that conformational changes of surface bound biomolecules can be measured and used analytically.

10:40am **BI-MoM8 Study of Metal Film-Tethered (Bio)Molecules in Aqueous Solution by Enhanced ATR-IR Spectroscopy***, **D.P. Land**, J.S. Toofan, C.M. Gerth,* University of California, Davis

Data are presented illustrating the application of overlayer-enhanced attenuated transmission-Fourier transform infrared spectroscopy (E-ATR-FTIR). The presence of a thin metal film at in internal reflection interface accomplishes several important feats. It enhances and concentrates the electric field in the near-surface region. It introduces a wide range of chemical possibilities for surface modifications by which analytes can likewise be concentrated near the interface. And it minimizes interactions with the bulk solvent, facilitating the use of IR spectroscopy in aqueous (and other) solutions. The combination of effects facilitates the study of numerous solution systems, and most importantly, perhaps, aqueous solutions. The experiment has been modeled to reveal details of the dependence upon prism material (ZnSe and Ge), thin film thickness and composition (metals and oxides), as well as angle of incidence and adsorbate properties. Experimentally, several key experiments have been performed. Data will be shown which includes the study of reactions of thiols with the gold films, in aqueous and other solutions. Additionally, spectra for tethered proteins, antibodies, and protein-antibody reactions have already been acquired and will be presented. Detection limits in the tens of femtomoles for proteins and antibodies has been achieved. Experiments currently underway include reactions of enzymes with tethered inhibitors and of tethered enzymes with substrates and co-factors.

11:00am **BI-MoM9 Investigation of Fibrinogen Displacement from Oxide Surfaces***, **P.S. Cremer,*** Texas A&M University **INVITED**

This talk will discuss the adsorption and displacement of fibrinogen at the silica/aqueous interface. It has been known since Leo Vroman's original studies in 1969 that fibrinogen is one of the first proteins to adsorb from human plasma on oxide surfaces, but it is ultimately displaced by other smaller and less abundant species in solution. We have employed a combination of vibrational sum frequency spectroscopy (VSFS), atomic force microscopy, immunoassays, and kinetic studies to unravel the molecular level details of the mechanism for this process. The results reveal that lysine and arginine residues on the protein's alpha-C domains interact with the surface via weak electrostatic binding. The rest of the protein can only make stronger hydrogen bonding and hydrophobic contacts once these domains have been displaced. In particular, the VSFS data give direct evidence for alignment of arginine and lysine residues with the surface in the protein's most displaceable configuration.

11:40am **BI-MoM11 Probing the Conformation of Hydrated Molecular Adsorbates on Solid Interfaces Using Long Period X-ray Standing Wave Fluorescence***, **C.A. Crot**, C. Wu, M. Schlossman,* University of Illinois at Chicago*; T.P. Trainor,* University of Alaska*; P.J. Eng,* University of Chicago*; L. Hanley,* University of Illinois at Chicago

Understanding the process of protein and biomolecular adsorption onto solid surfaces is of great importance in a wide variety of applications including biomaterials, tissue engineering, biosensors, immunoassays, and protein arrays. However, direct investigation of adsorption processes and the hydrated conformation of a molecular adsorbate is difficult since the majority of surface analysis techniques require ultra-high vacuum conditions. In this work long period x-ray standing wave fluorescence spectroscopy (XSW) is being developed as a spatial probe of molecular adsorption at the liquid-solid interface using a model surface-adsorbate system. A 25 nm thick polystyrene layer is spin coated on a thick silicon wafer, then the top of this layer is amine-functionalized via hyperthermal allyl amine ion deposition. X-ray photoelectron spectroscopy and atomic force microscopy are used to monitor the chemistry and morphology of this amine-polystyrene model surface. A thirteen residue peptide is covalently bound to a poly(ethyleneglycol) chain that is terminated with a bromine labeled amino acid and used as the model adsorbate. This Br-PEG-peptide construct is adsorbed onto the amine surface and its hydrated conformation is examined by XSW and x-ray reflectivity. Measurements of the bromine fluorescent yield as a function of incident angle provides information on the distance of the bromine layer from the silicon surface with an accuracy of several angstroms. Preliminary data analysis of the Br-PEG-peptide conformation indicates the peptide end is adsorbing directly onto the amine surface while the bromine atom on the Br-PEG end is extended ~13@+-@3 nm from the amine surface into the aqueous layer. Adsorbate configuration is probed as a function of adsorption time, amine film characteristics, and other experimental parameters. The general applicability of the XSW technique to probe the conformation of labeled adsorbates at the aqueous-solid interface is discussed.

Materials Solutions for Cooling Technology Topical Conference
Room 303B - Session CT+TF-MoM
Thermal Transport in Thin Films and Nanostructured Materials

Moderator: D. Cahill, University of Illinois, Urbana-Champaign

8:20am **CT+TF-MoM1 Impact of Electron-Phonon Coupling on Thermal Boundary Resistance by Molecular-Dynamics Simulation***, **R.J. Stevens**, P.M. Norris,* University of Virginia

With the growing interest in ULSI circuits and superlattices, an increasing need to understand thermal transport mechanisms across interfaces has become necessary. As the density of interfaces rapidly increases, device level thermal management is no longer dominated by the thermal properties of the individual layers but rather the thermal boundary resistances (TBR). Unfortunately, our current understanding of room temperature TBR is not adequate for proper thermal design of interface dense devices. Most TBR theoretical work has been an extension of the acoustic mismatch theories and has been limited to phonon elastic scattering processes for perfect interfaces. Other transport mechanisms have been considered such as electron-phonon (e-p) scattering and inelastic phonon scattering. There has been very little effort to systematically measure room temperature TBR and verify the proposed theories. Unfortunately, measuring TBR is quite difficult, although there has been some success using ultrafast spectroscopy techniques. Alas, it is problematical to systematically fabricate and fully characterize a series of interfaces and validate the proposed models. Molecular-dynamics simulations (MDS) can enhance existing experimental work by allowing analysis of controlled and well-defined interfaces. MDS enable the ability to alter material properties and atomic-level structure of the interface, so the mechanisms of TBR can better be understood. In this work, we perform MDS of the energy transport through an interface of a Si â?" metal system described by semi-empirical potentials (Stillinger-Weber and Embedded Atom Method). The electronic heat conduction in the metal film and e-p coupling are included by using a recently developed model that combines MD with a continuum description of the evolution of the electron temperature. The electron scattering contribution to TBR is determined by altering the e-p coupling strength in the bulk and at the interface.

8:40am **CT+TF-MoM2 Thin Film SiGe Superlattice Micro Refrigerators Flip-Chip Bonded with IC Chips***, **Y. Zhang**, A. Shakouri,* University of California, Santa Cruz*; G. Zeng,* University of California, Santa Barbara*; P. Wang, A. Bar-cohen,* University of Maryland

Thin film SiGe-based superlattice micro refrigerators, with device sizes ranging from 40-150 micron in diameter, have demonstrated cooling by 4.5C at ambient temperature and cooling power density exceeding 500W/cm2. In this talk we present theoretical and experimental study of these thin film refrigerators flip-chip bonded underneath 50 micron thick silicon substrate. The idea is to evaluate the effectiveness of these refrigerators to eliminate hot spots in IC chips without modifying the IC processing steps. Even though the 50 micron thick silicon has relatively high thermal conductivity and the cooling of micro refrigerators is spread over larger areas, theoretical studies show that localized cooling by 1-2C with cooling power density exceeding 100W/cm2 should be possible. Experimentally three micron thick gold-to-gold bonding is used to attach the two wafers. Cooling on top of the silicon heat load wafer is measured using microthermocouples. Thin film resistor heaters are used to evaluate the cooling power density. We have achieved cooling power density ~40W/cm2. It is interesting to note that even though bare microrefrigerators have an optimum size for maximum cooling on the order of 70 microns in diameter and largest cooling power density is obtained with the smallest devices, in the two-chip bonded configuration, the biggest coolers have the largest cooling and the cooling power density is not a strong function of the size. 3D electrothermal simualtions are used to explain the measured results and to evaluate maximum cooling performance under various ideal and non-ideal conditions.

9:00am **CT+TF-MoM3 Interfaces, Functionalization and Heat Flow in Nanoscale Materials.***, **S. Shenogin**, A. Bodapati, L. Xue, P. Keblinski,* Rensselaer Polytechnic Institute

The influence of the interface resistance on heat exchange between carbon nanotubes (CNs), fullerenes and embedding soft material medium was studied by means of molecular dynamics simulation. Due to a weak coupling between thermal vibrations of stiff carbon nanostuctures and soft organic matrix, the inclusion-matrix interface has high thermal resistance (Kapitza resistance). Recent experiments and simulations showed that the resistance of such interfaces is equivalent to the matrix layer with thickness 5 to 20 nm@footnote 1@,@footnote 2@. High boundary resistance considerably reduces thermal conductivity of the nanotube-based polymer composites and limits potential heat management applications. Our simulation shows that chemical functionalization of the nanoparticles with short organic chains reduces the interface thermal resistance by enhancing interactions between nanoparticels and the matrix. Detail dynamical analysis demonstrates that functionalization widens the overlap between the vibrational spectra of carbon nanostructures and the matrix. Remarkably, in the case of fullerenes, functionalization with a single chain reduces interfacial resistance by a factor of ~ 5. In the case of CN the interface resistance is reduced 4 times when 7 or more % of carbon atoms are functionalized. However, the functionalization decreases the intrinsic high thermal conductivity along the nanotube. The selection of the optimal side group length and concentration will be discussed. @FootnoteText@ @footnote 1@ S.T Huxtable et. al., Nature Materials, 2, 731 (2003).@footnote 2@ S.Shenogin et. al, J.Appl.Phys 95 (12), (2004).

9:20am **CT+TF-MoM4 Thermal Transport in Nanostructured Materials***, **D. Cahill**,* University of Illinois, Urbana-Champaign **INVITED**

The thermal conductance of interfaces is a key factor in controlling the thermal conductivity of materials with high densities of internal interfaces, e.g., nanocomposites, nanocrystalline ceramics, and short-period multilayer films and superlattices. Low interface conductance puts a lower limit on the size of nanoparticles that can be used as fillers in thermal interface materials and limits the increases in the the thermal conductivity that can be achieved in carbon nanotubes composites. We study these effects using high-precision measurements of thermal conductivity using the 3-omega method and psec transient absorption measurements of the thermal decay time of carbon-nanotubes suspended in micelles in water. We have also recently advanced the state-of-the-art of time-domain-thermoreflectance (TDTR) measurements of thermal transport and are using TDTR to study heat transport across individual interfaces and the thermal conductivity of sputtered multilayers. The thermal conductance of epitaxial interfaces between similar materials approaches the high values predicted by simple theory. Nanolaminates of dissimilar materials show remarkable reductions in thermal conductivity when the layer thickness is a few nm; this approach provides a novel materials with ultra-low thermal conductivity without sacrificing strength or environmental protection.

10:00am **CT+TF-MoM6 Thin Film Micro Refrigerators for on Chip Thermal Management***, **A. Shakouri**,* University of California at Santa Cruz **INVITED**

In this talk, we review design considerations for high cooling power density thermoelectric/thermionic coolers. Conventional bismuth telluride-based thermoelectric modules have a maximum cooling of about 70° C, however the cooling power density is low, on the order of 1-10 W/cm2. The micro and nanoscale electronic devices can generate thousands of watts per centimeter square heating, which is far beyond the capability of current TE modules. The maximum cooling power density of a TE module is inversely proportional to the length of its elements (distance between hot and cold junctions). Thus it is possible to increase the cooling power density with the use of thin film material. 100 micron thick Peltier modules with cooling power density exceeding 100W/cm2 have been demonstrated. Further increase requires significant improvement in metal-semiconductor contact resistance and in heat sink thermal resistance. An alternative solution is to use the thermoelectric properties of silicon or III-V substrate material. Heat and current spreading in 3D electrode configuration, allow removal of hot spots in IC chips. Furthermore, addition of a 1-5 micron thick superlattice can improve the cooling performance by increasing the selection between hot and cold carrier transport via thermionic emission and by reducing thermal resistance between hot and cold junctions. Several III-V and silicon heterostructure integrated thermionic (HIT) microcoolers have been fabricated and characterized. They have achieved cooling, on the order of 4.5° C at room temperature and 12° C at 200° C ambient temperature. Cooling power density was also characterized and values ranging from 100-680W/cm2 were measured. Finally, an optical technique based on thermoreflectance imaging was used to obtain temperature distributions on top of devices with sub micron spatial resolution and <0.1° C temperature resolution.@footnote 1@ @Footnotetext@ @footnote 1@ Work supported by DARPA and ONR MURI.

10:40am **CT+TF-MoM8 Micro- and Nanoscale Thermal Phenomena in Magnetic Recording Heads***, **Y.S. Ju**,* UCLA **INVITED**

Advances in magnetic recording heads are critical in enabling continued growth in areal densities of magnetic data storage. In the present talk we review studies of thermal characteristics of recording heads at micro- and nanoscales, which strongly affect their performance and reliability. Geometric scaling of GMR (giant magnetoresistance) and TMR (tunneling magnetoresistance) sensors leads to significant increase in temperature rise per unit power, which limits maximum permissible bias current and increases electrostatic discharge (ESD) susceptibility. This motivates fundamental studies of thin film thermal conductivity, thermal interface resistance, and heat generation due to electron tunneling. Reliability of magnetic recording heads is also compromised by thermal protrusion and thermal creep flow induced by Joule heating in write heads. Spatial distribution of eddy current heating in magnetic yoke structures and heat transfer across air bearing are important factors influencing thermomechanical behavior of recording heads and reliability of head-disk interface. Fundamental understanding of thermal phenomena in magnetic recording heads will also play an important role in the development of thermally-assisted recording, which is a promising approach to extending magnetic recording beyond the superparamagnetic limit of conventional recording media.

11:20am **CT+TF-MoM10 Transport and Mechanics in Hard and Soft Nanomaterials***, **A. Majumdar,*** University of California, Berkeley **INVITED**

Hard and soft materials are characterized by the ratio of their respective binding energies (Eb) with respect to thermal fluctuations that are characterized by kT. Mechanics and dynamics of hard materials (Eb >> kT) are generally unaffected by kT, except when undergoing irreversible processes such as transport phenomena or inelastic deformations. On the other hand, fluctuations dominate the behavior of soft materials (Eb ~ kT) such as liquids and biomolecules, where entropic forces are critical in their mechanics. As part of this lecture, I will focus on two topics, both of which relate to the interplay between entropic and elastic forces: (i) Transport of heat and fluid in solid nanostructures such as nanotubes and nanowires. I will share some of our recent discoveries of how heat and charge transport in such nanostructures can be manipulated by size confinement and interface engineering; (ii) Actuation of mechanical devices such as cantilever beams using reactions of biomolecules (eg. DNA hybridization, antigen-antibody binding). I will also discuss the implications of our work on energy conversion and biomedical technologies.

MEMS and NEMS
Room 213C - Session MN-MoM
Processing and Characterization for MEMS and NEMS

Moderator: S.L. Firebaugh, United States Naval Academy

8:20am **MN-MoM1 Porous Thin Films for MEMS and Nano Applications***, **C.J. Kim,*** University of California, Los Angeles **INVITED**

The talk will summarize various porous thin-films developed at the UCLA Micro and Nano Manufacturing Laboratory over the past several years. (1) Micromachining of aerogel-like thin film has been developed, including photolithographic steps and surface micromachining procedures for silica and alumina. Mechanical properties have been measured by direct bending tests with such fabricated free-standing aerogel microbeams. (2) Polysilicon thin film on silicon dioxide, which represents a typical surface micromachining process, has been converted permeable by post-deposition electrochemical etching, allowing on-chip vacuum encapsulation of micro and nano structures finally practical. (3) Silicon wafer with high-aspect-ratio pores serves as a mold in developing three-dimensional nanobatteries. Although most projects start from development of pore formation processing steps, the main goals for all are to explore specific new applications that take advantage of the unique property of the materials or the processing procedures.

9:00am **MN-MoM3 Nanotribological Characterization of Perfluoropolymer Thin Films for BioMEMS Applications***, **K. Lee**, B. Bhushan, D. Hansford,* The Ohio State University

The undesired adhesion of micro-organisms and biomolecules to surfaces and biofilm development called biofouling may cause detrimental effects to the performance of most biomedical microelectromechanical system (BioMEMS) devices. A vapor phase deposition technique to modify surfaces with perfluoropolymer and silane thin films was developed to reduce or prevent protein or cell interactions, critical for their use. The surface properties of these devices and therefore the surface modifications become increasingly important for BioMEMS applications as the channel dimensions decrease within these systems. Compared to dip coating or spin coating, the vapor phase deposition is more effective for smaller channels, especially at the nanoscale. Since nanotribological behaviors such as surface topography, adhesive and frictional properties and mechanical stability of these films play a very important role in forming uniform, conformal and ultra thin films on the surface and reducing protein or cell interactions, coating effects of these films were characterized extensively using an atomic force microscopy in this study.

9:20am **MN-MoM4 Multi-scale Friction Experiments Using Atomic Force Microscopy and Surface Micromachined Interfaces***, **E.E. Flater**, M.D. Street,* University of Wisconsin-Madison*; A.D. Corwin, M.P. de Boer,* Sandia National Laboratories*; R.W. Carpick,* University of Wisconsin-Madison

Friction and wear are major limiting factors for the development and commercial implementation of devices fabricated by surface micromachining techniques. We use atomic force microscopy (AFM) to determine the constitutive relation for friction for a single asperity nanoscale contact on micromachined surfaces. Friction is measured using AFM SiO@sub2@- and alkyl-monolayer terminated tips sliding on alkyl-terminated single crystal silicon. The alkyl monolayer coatings include octadecyltrichrolosilane (OTS), octadecene, and fluorinated monolayers (FOTAS). Frictional information at the nanoscale is then used to predict tribological properties of a polycrystalline silicon nanotractor device interface. This microscale friction and wear test device provides abundant, quantitative information about friction and wear at an actual microelectromechanical system (MEMS) interface. This in-situ approach to measuring tribological properties of MEMS, combined with high-resolution atomic force microscope images of device wear, provides insight into the effects of wear and prescriptions for avoiding it.

9:40am **MN-MoM5 Deposition and Characterization of Nitrogen-Doped Polycrystalline SiC Films for MEMS Applications**, *J. Trevino, X.-A. Fu, S. Rajgopal, M. Mehregany, **C.A. Zorman**,* Case Western Reserve University

This presentation reports on the development of processes to deposit undoped and nitrogen-doped, polycrystalline silicon carbide (poly-SiC) films on large-area substrates in a high-throughput, low pressure chemical vapor deposition (LPCVD) reactor using SiH2Cl2, C2H2 and NH3 precursor gases. The films were deposited in a customized deposition system constructed around a resistively-heated, horizontal furnace similar in design to a conventional polysilicon furnace and capable of holding up to 100, 150 mm-diameter substrates. To the best of our knowledge, this is the largest furnace designed specifically for the production of poly-SiC films for MEMS. Depositions were performed on 100 mm-diameter Si and SiO2-coated Si wafers using a SiH2Cl2 flow rate of 35 sccm, a C2H2 (5% in H2) flow rate of 180 sccm and NH3 (5% in H2) flow rates ranging from 10 to 90 sccm. The furnace temperature was held at 900C while the deposition pressures ranged from 2.5 to 4 Torr. Stoichiometric poly-SiC films were deposited over this entire range. The films exhibit a strong (111) 3C-SiC texture regardless of pressure. Films having a thickness of up to 2 microns are uniform, with less than a 5% variation across both the wafers and the boat. Four-point probe measurements indicate that the highest conductivities are achieved at a NH3 flow rate of 90 sccm. Wafer-scale residual stresses were measured using an optical curvature measurement technique. The residual stresses in the heavily-doped films are tensile with values decreasing to around 100 MPa in films deposited at 4 Torr. Single-layer, surface mechanical properties test structures, such as cantilever beams, stress pointers and lateral resonators were fabricated, successfully released and used to characterize the films. Likewise, bulk micromachined membranes were fabricated and tested using a load-deflection technique. Stress measurements from these micromachined structures confirm the wafer-scale residual stress measurements.

10:00am **MN-MoM6 Characterization of Nanotribological Properties and Surface Chemistry of Advanced Nanostructured Carbon Materials for MEMS and NEMS Applications***, **A.V. Sumant**, D.S. Grierson,* University of Wisconsin-Madison*; J.E. Gerbi,* Argonne National Laboratory*; J.P. Birrell,* Argonne National Laboratory, U.S.*; J.A. Carlisle, O.H. Auciello,* Argonne National Laboratory*; T. Friedmann, J.P. Sullivan,* Sandia National Laboratories*; R.W. Carpick,* University of Wisconsin-Madison

Despite rapid advances in micro- and nanofabrication technologies, the implementation of reliable, high endurance devices that involve sliding contacts remains elusive. At small length scales, device properties are dominated by surface chemistry rather than bulk properties, and therefore materials with superior tribological properties and optimized surface chemistry are needed. Ultrananocrystalline diamond (UNCD) and tetrahedra amorphous carbon (taC) thin films have exceptional physical, chemical and tribological properties at the macroscale (nearly equivalent to those of single crystal diamond) and are being considered promising materials for the fabrication of high performance MEMS devices. However, little is known about the surface chemistry of these materials, and how it affects their nano- and micro-scale tribological performance. We have developed detailed methodologies to characterize nanotribological properties and surface chemistry of UNCD and taC at the tribologically relevant interface by using a combination of near-edge X-ray absorption fine structure spectroscopy (NEXAFS), Auger electron spectroscopy (AES), X-ray photoelectron spectroscopy (XPS), and atomic force microscopy (AFM). We show that the surface chemistry, sp2-sp3 ratio, and nanoscale friction and adhesion can be different on the etched underside of the film (the side which becomes exposed and makes tribological contact after a MEMS release process) as compared with the top side of the film. We also discuss the effect of hydrogen plasma treatment, which in the case of UNCD renders the surface extremely inert and chemically pure, and reduces nano-scale friction and adhesion dramatically. Adhesion, as measured with tungsten carbide AFM probes, is reduced to the van der Waals limit indicating full saturation of dangling surface bonds and elimination of surface contaminants.

10:40am **MN-MoM8 Critical Issues in Epitaxial Growth of Pulse Laser Deposited AlN Films for MEMS and NEMS based RF Resonators***, **S. Hullavarad**, R. Vispute, T. Venkatesan,* University of Maryland*; A. Wickenden, L. Currano, M. Dubey, T. Takacs, J. Pulskamp,* U.S. Army Research Laboratory

AlN exhibits strong piezo-electric properties suitable for RF resonator applications. In this work we report the growth of highly oriented AlN films for MEMS and NEMS resonator devices. A multiple flexural structure of Pt/SiO2/Si is used as a substrate and films are grown by Pulse Laser Deposition (PLD) technique at a pulse energy of ~2J/cme2 with a repetition rate of 10 Hz. The process is optimized for the growth of AlN on different thicknesses of underlying SiO2. The films are characterized by XRD, RBS and techniques for crystalline quality and stoichiometry respectively. The interface analysis of underlying structures is analyzed in detail by RBS and oxygen content in the film is monitored by Resonant Oxygen Scattering technique. The morphology of AlN films is studied by scanning electron and atomic force microscopies. We have obtained highest Q factors for PLD grown AlN MEMS resonator beams of Q = 8,000 at fo = 2.5 MHz and Q = 17,400 at fo = 0.44 MHz We also address in this work critical issues related to (1) thickness of SiO2 (2) method of growth of SiO2 in fabricating MEMS and NEMS devices. These factors are very essential for the growth of high quality AlN films. However, SiO2 provides a amorphous underlayer for the growth of AlN leading to non in plane aligned AlN with respect to substrate. A lattice matching, epitaxial oxide layer like Y2O3 in place of SiO2 is going to be a unique solution for eventual epitaxial growth of AlN. We address the epitaxial issues of AlN and underlying oxide for improving the resonator properties of AlN based MEMS and NEMS devices.

11:00am **MN-MoM9 Vapor Phase Uptake of Mobile Organophosphates for MEMS Lubrication Purposes***, **D.A. Hook**, W. Neeyakorn, C. Jaye, J. Krim,* North Carolina State University

MEMS devices are highly susceptible to surface forces that can cause suspended members to deflect towards the substrate, collapse and/or adhere permanently to the substrate. A number of surface treatments have met with varying degrees of success for alleviation of MEMS-related stiction/adhesion problems, but friction and wear remain problematic. We report here the results of a quartz crystal microbalance (QCM) study of the nanodynamics and uptake characteristics of organophosphate (tricresylphosphate and t-butyl phenyl phosphate) layers adsorbed from the vapor phase onto silicon and silane treated silicon surfaces. Silanes applied from the liquid phase as self-assembled monolayers are in common use as anti-stiction treatments for silicon MEMS devices, but degrade at elevated temperatures. Organophosphates are highly stable at temperatures in excess of 600ï,°C, act as antioxidants, and have well-documented tribological performance for certain materials combinations. We observe that organophosphates adsorb readily onto selected silanes. The silane +organophosphate combinations moreover exhibit interfacial slippage and/or viscoelasticity in response to the oscillatory motion of the QCM. Such effects have previously been linked to beneficial tribological performance.[1] Work is in progress to assess the tribological performance of these materials on actual MEMS devices. Work supported by AFOSR and NSF. @FootnoteText@ @footnote 1@M. Abdelmaksoud, J.Bender and J. Krim, Phys. Rev. Lett. 92, 176101 (2004).

11:20am **MN-MoM10 Mechanical and Electrochemical Characterization of Gold Membranes on a Drug Delivery MEMS Device***, **Y. Li**, M.J. Cima,* Massachusetts Institute of Technology

Our drug delivery MEMS device was designed to release multiple substances with complex profiles in order to maximize the efficacy of drug therapies. The device consists of arrays of microreservoirs etched into a silicon substrate to contain different types and doses of drug. The release of drug is achieved through the electrochemical dissolution of the gold membranes that seal individual reservoirs. The mechanical and electrochemical properties of the gold membranes are important parameters in evaluating the reliability of device performance. A bulge test apparatus was constructed to measure the mechanical properties of the gold membranes. The apparatus is pressurized, and the resutling deflection of the membranes is measured using interferometry. The biaxial modulus of elasticity and residual stress in the membranes extracted from the bulge test were 126-168 GPa and ~100 MPa (tensile) respectively for membranes with in-plane sizes ranging from 20 to 200 mm. An in situ experimental set up was constructed to observe the electrochemical disintegration process of the gold membranes when voltage was applied. The bulge test was used to evaluate the mechanical integrity of gold membranes corroded for different duration of time. The decrease in the membrane burst pressure with longer corrosion time under the bulge test confirmed a gradual loss of mechanical integrity of the gold membranes due to corrosion. Observation of the membrane morphology with an optical profiler indicated an abrupt transition in the membrane stress state from slightly tensile to highly compressive after five seconds of corrosion. This suggests that the gold membrane disintegration occurs by a combination of thinning through active dissolution and accumulation of compressive stress.

11:40am **MN-MoM11 Microfabrication and Nanomechanical Characterization of Polymer MEMS for Biological Applications***, **G. Wei**, B. Bhushan, N. Ferrell, D. Hansford,* The Ohio State University

Polymer Microelectromechanical System (MEMS) devices are promising for biological applications such as development of biosensors and biomechanical devices. The relatively low stiffness and improved biological interface between cells and polymeric materials make polymer cantilever and beam structures attractive as highly sensitive force sensors for measuring cellular and biomolecular nanomechanics. In order to develop polymer Bio-MEMS, novel polymer microfabrication techniques are required, and the nanomechanics studies including measurement of the mechanical properties of the polymer materials in the nano scale must be carried out. This paper presents the development of soft lithography based polymer Bio-MEMS microfabrication techniques and systematic studies on the nanomechanical characterization of the polymer materials, polymer beams and polymer cantilevers. Poly (methyl methacrylate) (PMMA) and poly (propyl methacrylate) (PPMA) are used to make the polymer beams and cantilevers, which are 5 µm wide, 10-30 µm long and 200 nm-5 µm thick, for MEMS integration. The hardness, creep behavior and scratch resistance of the PMMA and PPMA microstructures were measured using nanoindentation/nanoscratch technique with a Nano Indenter II system, and the nanomechanical properties are compared with the bulk values. The elastic modulus of the polymer beam was obtained from the bending tests performed by nanoindentation, and the nano scale fatigue of the polymer cantilever was measured using the nanoindentation Continuous Stiffness Measurement (CSM) technique. To simulate the working environment of the polymer Bio-MEMS, PMMA and PPMA beams and cantilevers were also placed in an aqueous solution (saline, DI water, etc.), and nanoindentation experiments were performed on such samples. The results are discussed along with the dry condition values.

Nanometer-scale Science and Technology
Room 213D - Session NS-MoM

Carbon Nanotubes-Electrical Properties

Moderator: M.C. Hersam, Northwestern University

8:40am **NS-MoM2 Quantitative Analysis of Electronic Properties of Carbon Nanotubes by Scanning Probe Microscopy: from Atomic to Mesoscopic Length Scales***, **V. Meunier**, S.V. Kalinin, J. Shin, A.P. Baddorf, R.J. Harrison,* Oak Ridge National Laboratory

Scanning Probe Microscopy techniques are the key to real space imaging of electronic transport properties, including the electrostatic potential distribution and local field effects, in low-dimensional systems. The interpretation of SPM data in terms of the local electronic properties of 1D systems such as carbon nanotubes requires quantitative analysis of the tip-nanotube interactions. Here, the electrostatic interactions between a point charge and a carbon nanotube are studied using a combination of first principles density functional calculations and continuum electrostatics modeling. The atomistic first principles investigation is extended to mesoscopic length scales by matching to a continuum electrostatic approach. Furthermore, realistic tip shape effects are included using an image charge model. An approach for the measurement of tip radius of curvature from the electrostatic SPM data is presented. Within this approach, we can quantitatively describe, for the first time, the capacitive tip-surface interactions and predict the magnitude of the tip gate effect in nanoscale systems, such as carbon nanotubes and semiconductor nanowires.

9:00am **NS-MoM3 Electronics and Optoelectronics with Single Carbon Nanotubes*, P. Avouris,*** IBM T.J. Watson Research Center **INVITED**

Carbon nanotubes (CNTs) are 1D nanostructures with unique properties that recommend them for applications in future nanoelectronics and optoelectronics. I will discuss the electronic structure and electrical properties of semiconducting carbon nanotubes and the fabrication and performance of nanotube devices. Transport experiments and simulations will be used to determine the switching mechanism of nanotube transistors, the nanotube-metal interactions and the role of the ambient environment on the transistor properties. I will then discuss how these findings can be utilized to produce high performance p-, n- and ambipolar nanotube field-effect transistors (CNTFETs) and logic circuits. Semiconducting CNTs are direct gap materials. This, plus their 1D character have important implications for their optical properties. I will first discuss the nature of the excited states of CNTs. I will show that CNTs form strongly bound 1D-exciton states and discuss the scaling properties of these excitons. Spectra obtained by recording the photocurrent of single CNTs employed as channels of CNTFETs will be presented. I will then show that an ambipolar nanotube field-effect transistor can act as a single molecule, electrically-driven light source. The spectra, polarization and the dependence of the light intensity on applied bias will be used to prove that the light is generated through radiative e-h recombination in the CNT. Spatially-resolved studies of the emission as a function of applied bias will be used to map the boundaries of the electron and hole currents and to determine the recombination lengths. These results show that a CNTFET is a particularly versatile molecular device that can be used, depending on the bias conditions, as a high performance electrical switch, a light detector or a light source.

9:40am **NS-MoM5 Ballistic Transport of Hole in 4µm Carbon Nanotube Channel Transistor with Coulomb Blockade Effect*, K. Matsumoto,*** Osaka University, Japan

We have succeeded in observing the coexistence of the ballistic transport and Coulomb blockade effects of hole in the carbon nanotube channel transistor. The carbon nanotube was grown by the thermal chemical vapor deposition. After the growth of carbon nanotube, the source, drain, gate electrodes were formed. The distance between the source and drain electrode is 4µmm, that means the effective channel length of carbon nanotube is 4µmm. The sample was measured at 8.6K. The dependence of the drain current on the gate bias shows the periodic Coulomb oscillation and Coulomb diamond characteristics with the periods of 150mV. The drain current decrease with the increase of the gate bias, which means the carrier is hole. From the size of the Coulomb gap, the total charging energy was estimated to be as small as 3.1meV. From this charging energy, the length of the island was estimated to be about 4µmm, which coincides with the carbon nanotube channel length. This fact means that the entire carbon nanotube works as one island for the Coulomb blockade effect for the hole. At the outside of the Coulomb blockade regions, the drain current shows the negative differential conductance with the periods of as small as 400µmV. This negative differential conductance is attributed to the resonant tunneling of the hole through the quantum confinement state formed inside the carbon nanotube. From the periods of the negative differential conductance, the length of the quantum well formed inside the nanotube was calculated to be as large as about 4µmm, which again coincides with the entire carbon nanotube channel length. This result means the quite important facts that the quantum confinement state is formed in the entire carbon nanotube and tunneling barrier is formed at the source and drain electrodes. Therefore, hole can transport ballistically through entire carbon nanotube channel of 4µmm by keeping the coherency of the hole wave.

10:00am **NS-MoM6 Carbon Nanotube Photo-detectors*, M.S. Marcus*,** *O.M. Castellini, J.M. Simmons, M.A. Eriksson,* University of Wisconsin-Madison

We demonstrate two different nanotube device structures for use as photo-detectors: Bundle devices on quartz using photo-generated currents in the bundle, and transistor devices on Si/SiO@sub 2@ substrates that use photo-generated voltages in the substrate to provide a gating effect. The transistor devices are fabricated on SiO@sub 2@/p-Si substrates, where the p-Si is used as a gate for the nanotube channel. Light is absorbed by not only the carbon nanotube producing photocurrents, but also in the silicon gate that produces a photo-voltage at the interface between the Si/SiO@sub 2@. We observe that photo-voltages of ~15mV change the channel current by up to 1nA in the transistor. The small addition of the photo-voltage when the nanotube is illuminated by a modulated light source acts to probe the derivative of the channel current with respect to the gate voltage. When the laser illuminates at large distances from the nanotube we find that there are smaller but still measurable changes in the channel current, indicating that the carriers responsible for photo-gating are mobile. In order to isolate the nanotube-light interaction from the silicon gate, we have fabricated nanotube bundle devices on transparent quartz substrates. We measure a variety of response times, some of which are surprisingly slow sometimes taking ~8ms to transition from a light off to on state. We propose that inter-tube coupling plays a role in the long response times, and present a model of why it can take photo-generated carriers a long time to be extracted as photocurrent.

10:20am **NS-MoM7 Field Electron Emission from Aligned Carbon Nanotube Bundles at an Ultra-Low Threshold of 1 V/µm*, K.-Y. Lee*,** *M. Katayama, N. Hayashi, Y. Terao, T. Miyake, K. Himuro, S. Honda, J.-G. Lee,* Osaka University, Japan*; T. Hirao,* Kochi University of Technology, Japan*; H. Mori, K. Oura,* Osaka University, Japan

To realize a practically applicable field electron emitter made of carbon nanotubes (CNTs), it is desirable to enhance the electric field concentration determined by the aspect ratio and number density of the individual CNT. As predicted theoretically, the field emission from an aligned CNT array becomes maximum when the ratio of intertube distance to the height of each individual CNT is about 2. We have succeeded in fabricating an architecture that satisfies such an optimal condition by using pillars of aligned CNT bundles. This provides a promising method of obtaining the optimal ratio of interpillar distance (R) to pillar height (H). Patterns of 50 µm diameter and 250 µm pitch of the Fe(5 nm)/Al(10 nm) multilayer catalyst were fabricated on a Si substrate by photolithography and sputtering. The pillars of aligned CNT bundles were grown on the patterns at 700°C by thermal chemical vapor deposition with C@sub 2@H@sub 2@ under a pressure of 600 Pa. Each pillar was composed of CNTs with a number density of about 10@super 10@ cm@super -2@. To obtain the optimal R/H of 2, the pillar height of about 125 µm was adopted. The pillar array exhibited a striking field emission characteristic. The threshold field needed to produce a current density of 10 mA/cm@super 2@, E@sub th@, was 1.0 V/µm. The obtained E@sub th@ is extremely low compared with those for other materials that have been reported so far. Monitoring the electron field emission by means of a fluorescent screen demonstrated the emission uniformity. More details of the results on field emission characteristics, and SEM, TEM observations of the carbon nonotube bundles will be presented.@footnote 1@ This work was partly supported by the Handai Frontier Research Center, and a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science, and Technology. @FootnoteText@ @footnote 1@M. Katayama, K.-Y. Lee, S. Honda, T. Hirao, and K. Oura, Jpn. J. Appl. Phys. (in press).

10:40am **NS-MoM8 Modeling of Gas-modulated Carbon Nanotube Schottky Barrier*, T. Yamada,*** NASA Ames Research Center

It is reported that the Schottky barrier between a semiconducting carbon nanotube (NT) and a metallic electrode is sometimes modified in the gaseous environment. There are three different cases: (1) there is no charge transfer between the gas and the NT/electrode (gas not charged) and the gas does not have a dipole moment (not polarized), (2) the gas is not charged, but is polarized, and (3) there is a charge transfer between the gas and the NT/electrode and the gas is charged. Case 1 will cause no Schottky barrier modulation. Case 2 will result in the Schottky barrier modulation through the modified work function in either the NT or the electrode due to the dipole moment in the gas. This is understood within the usual Schottky theory. Case 3 will also result in the Schottky barrier modulation, but depending on whether the NT and electrode are connected (closed) or not (open), the modulation is significantly different. The charged gas will attract the opposite charges in the NT and electrode. In the open circuit condition, the gas-NT and the gas-electrode interactions determine how much opposite charges are induced in the NT and electrode, respectively. However, in the closed-circuit condition, which is the usual condition in electronics applications, the induced opposite charges will move around the system and keep the Fermi level constant everywhere. This means that the induced opposite charges are redistributed in the NT and electrode. We have solved this redistribution problem and shown that the Schottky barrier modulation is large when the NT is in the depletion mode, while the modulation is negligible when the NT is consistently in the accumulation mode.

11:00am **NS-MoM9 Environmental Effects on Double Wall Carbon Nanotube Field Effect Transistors*, D. Kang,*** *W. Park,* Samsung Advanced Institute of Technology, Korea*; J.R. Kim,* Chonbuk National University, Korea*; C.J. Lee,* Hanyang University, Korea*; J.J. Kim,* Chonbuk National University, Korea

With the rise of nanotechnology, there are many new interesting properties induced by their dimensions and geometries. One of the these is large surface area due to their unique geometric shapes such as nanotube and nanowires. For device applications harnessing these materials, large surface area effects on electrical properties should be investigated for a better understanding of nano devices. Double Wall Carbon Nanotube(DWCNT)s could be the best material to investigate the effects because their small band gap should enhance the response to their environments. In this letter, we fabricate DW-CNTFETs in a back-gated structure and investigate environment effects on the electrical properties of DW-CNTFETs in comparison to SW-CNTFETs. Purified double wall CNTs (DWCNT) were suspended in a solvent and spin coated on SiO2 grown on a heavily doped Si substrate. Scanning Probe Microscopy (SPM) located the position of the wires on the substrate. After the pattern for metals contacts were generated by electron beam lithography, metal electrodes were defined by lift-off process after 100nm Pd metal evaporation. We find that DW-CNTFET shows conversion from unipolar to bipolar in vacuum. However, the SW-CNTFET does not show the conversion in the measurement conditions we used in this study. In ambient air, both CNTFETs shows large hysteresis by electron trapping at slow states. We believe that water adsorption on the tube plays an important role for ambipolar conversion.

11:20am **NS-MoM10 Electrical Characterization of Carbon Welds between Multiwalled Carbon Nanotubes*, P. Rice*,** *S.E. Russek, P. Kabos, R.H. Geiss,* NIST

Nanometer scale electronics based on carbon nanotubes have the potential to revolutionize the electronics industry by reducing circuit sizes dramatically and by increasing operational speed due to inherent properties of the nanotubes. Currently there are very few methods of connecting carbon nanotubes to electronics. The most prevalent so far is using the scanning electron microscope (SEM) focused at a junction between the nanotube and the circuit and growing a carbon contamination buildup we call a weld. This buildup, typical in most SEMs, is caused when the electron beam cracks carbon compounds commonly found on the surface of the sample and in the SEM atmosphere. The subsequent free and chemically active carbon quickly attaches itself to nearby surfaces and builds into mounds securely bonding the nanotube to the surface. Using microlithographic test structures we have measured the electrical characteristics of the nanotube and the welds from dc to MHz frequencies. These measurements have shown a semiconductor behavior of the nanotube and weld combination. To separate the weld electrical properties from the nanotube electrical properties we have built test structures that measure contact resistance between unwelded nanotubes and the same nanotubes after welding. Also, the molecular characteristics of the welds are very dependent on SEM parameters such as electron beam energy, alignment of the electron beam, vacuum pressure inside the SEM chamber, and molecular species near the beam impingement on the sample. We will correlate the structure of these welds to electrical properties as influenced by the SEM deposition parameters using transmission electron microscopy.

11:40am **NS-MoM11 Stiffness and Nonlinear Mechanical Properties of Single-Walled Carbon Nanotube Bundles*, P. Jaroenapibal,*** *D.E. Luzzi, S. Evoy,* University of Pennsylvania

Nanoscale cantilevered resonators offer great potential as sensing devices due to their high sensitivity to added masses or external forces. Highly-sensitive resonators can be accomplished by using long, thin, stiff, low density, and high quality cantilevers. Hybrid carbon nanotubes represent a powerful platform for the development of tunable nanoresonator-based devices that would provide both high quality resonance and sensing specificity. We have studied the mechanical properties of single-walled carbon nanotube (SWNT) bundles through in-situ transmission electron microscope (TEM) observation of mechanical resonance. The observed resonant frequencies of SWNT bundles ranged from 0.2 - 9 MHz, with resonance qualities Q ranging from 77 to 800. An effective Young's modulus of E* = 76 ± 4 GPa is extracted from the resonance data. This relatively low value indicates that the individual SWNTs are weakly interacting within the bundle, where slippage can occur due to the low sliding resistance between the atomically smooth surfaces of neighboring tubes. Departure from Lorentzian responses, an onset of non-linear behavior was observed under large actuation amplitudes. Specifically, bi-stable responses were observed in 4 µm long and 30 nm wide bundles when their end-point displacement approached a critical amplitude of x@sub c@ = 800 nm. Such non-linear behavior reveals the onset of inter-tube interactions within the bundle when sufficiently large bending is applied. We will discuss this non-linear data with respect to an effective Poisson ratio that results from inter-tube interactions, and describe the impact of beam irradiation on such interactions. Mechanical properties of hybrid carbon nanotubes in which fullerenes or other molecules are encapsulated will also be discussed.

Plasma Science and Technology
Room 213A - Session PS1-MoM
Low-k Dielectric Etching

Moderator: B. Turkot, Intel

8:20am **PS1-MoM1 Etching of SiC and SiCN with Tetrafluoroethane/Oxygen Reactive Plasma*, H.C. Galloway,*** Texas State University, us*; K.P. Radican,* Trinity College Dublin, Ireland*; J.M. McDonald, C. Martinez, D. Donnelly, D.C. Koeck,* Texas State University

Two materials, SiC and SiCN, are being increasingly considered as barriers for low dielectric constant materials in integrated circuit systems. It is important for researchers to be able to effectively remove these barrier layers to provide ohmic contact to the silicon substrate. The etch rate as a function of oxygen concentration was investigated in the RF magnetron plasma etching of SiC and SiCN with tetrafluoroethane gas. The etch rate and surface roughness were measured with atomic force microscopy, while evidence of polymer deposition or other surface contamination was analyzed with FTIR. Etch rates of > 10 nm/sec can be achieved with high selectivity with respect to an aluminum mask, and near infinite selectivity with respect to silicon. This process has been demonstrated to be compatible with producing test structures of aluminum contacts to measure the electrical properties of some low-k materials. Tetrafluoroethane is of interest due to its high fluorine content. It is also a nontoxic, ozone friendly gas with a short atmospheric lifetime. The role of oxygen in the etching process will be discussed and this etching process will be compared to other similar etches that have been previously reported.

8:40am **PS1-MoM2 Investigation of Fundamental Etching Reaction of Organic Low Dielectric Film Using Ion Beams with Radical Injection*, M. Yuuhei,*** *H. Masaru, G. Toshio,* Nagoya University, Japan*; A. Atsuhiro, T. Tetsuya,* Sony Co, Japan

Etching of organic low dielectric (low-k) interlayer films has been an essential process in ULSIs. However, this process becomes more complex and requires the high accuracy. Therefore, quantitatively understanding of this process is very important. Low-k etching using plasma, it is impossible to control the radicals and ions independently and so it is difficult to clarify the etching mechanism quantitatively. In this study, the ion beam apparatus with radical injection was developed and applied to the investigation of fundamental reaction of organic low-k film. The apparatus is composed of Ar@super +@ beam source, electron shower gun, and radical injection source. A compact electron cyclotron resonance plasma source was used as a radical source. To remove the electrons and ions in the plasma, two retard electrodes were installed in front of the plasma source. Using the vacuum ultraviolet absorption spectroscopy, the absolute densities of H and N radical generated by radical source were evaluated. Etching sample was blanket film of SiLKTM. The etching subsurface reactions were measured by in-situ XPS. The etch rate by Ar@super +@ beam was enhanced by the injection of H and N radicals. Especially, the etching rates of injection of mixing radicals of H and N were high comparing with those of H or N radical. The C=N/C-N ratio of subsurface was increased with increasing N radical and H+N radical density under the Ar+ ion bombardment When H+N radical was injected under the high ion energies above 300eV, the C=N/C-N ratio was higher than those under the low ion energies. Consequently, the high C=N/C-N ratio of the subsurface is a key factor for the high etch rate of the organic low-k film.

9:00am **PS1-MoM3 Fluorocarbon Surface Chemistry in Dual Frequency Capacitively Coupled Discharges for Dielectric Etching: A Comparison with Inductively Coupled Plasmas*, L. Ling*,** *X. Hua, L. Zheng,* University of Maryland at College Park*; G. Oehrlein,* University of Maryland at College Park, US*; E.A. Hudson,* Lam Research Corp.*; P. Jiang,* Texas Instruments Inc.*; P. Lazzeri, M. Anderle,* ITC-irst, Italy*; Y. Wang,* National Institute of Standards and Technology

Mechanically confined dual-frequency capactively coupled plasma (DFCCP) reactors featuring a high frequency powered electrode for plasma production and low frequency RF biasing for ion bombardment control of the substrate are increasingly being used for fluorocarbon (FC) plasma-based pattern transfer into SiO@sub 2@ and low k dielectric materials. We describe a study of confined DFCCP properties fed with C@sub 4@F@sub 8@/Ar and C@sub 4@F@sub 6@/Ar. In particular, we compare the chemistry of FC films formed on various surfaces with data obtained for inductively coupled discharges. Precursor gas dissociation is determined using mass spectrometry. The composition of the incident ion flux is determined by ion-sampling. The deposition rates, composition and bonding of passively deposited fluorocarbon films (no etching of the substrate), and the composition, bonding and thickness of the surface reaction layers that form on SiO@sub 2@, resist and silicon surface during steady state etching are determined as a function of processing conditions using ellipsometry and X-ray photoemission spectroscopy. The influence of ion bombardment on the composition of deposited fluorocarbon films is studied by comparing FC films deposited underneath a small gap structure with those deposited on ion bombarded surfaces. The influence of pressure, RF bias and gas mixture of FC-based DFCCP on the characteristics of resist pattern transfer into organosilicate glass and nanoporous silica is also reported.

9:20am **PS1-MoM4 Low-k and Porous Low-k Sidewall Roughening: Fluorocarbon Plasma and Beam Measurements*, Y. Yin*,** *S.A. Rasgon, H.H. Sawin,* Massachusetts Institute of Technology

For the patterning of sub 100 nm features, a clear understanding of the origin and control of line edge roughness (LER) is extremely desirable, both from a fundamental as well as a manufacturing perspective. Plasma etching processes often roughen the feature sidewalls, leading to the formation of anisotropic striations. It is this post-etch sidewall roughness which will ultimately affect device performance. The integration of organosilicate glass (OSG) and porous OSG films as low-k interlayer dielectrics presents new challenges from a roughening standpoint, particularly when using highly polymerizing fluorocarbon plasma chemistries typical of oxide etching. Under certain conditions the added carbon present in OSG films can increase localized deposition, yielding both carbon-rich and substrate-rich areas of the sample, and creating surface roughness based on the etch selectivity difference (polymer micromasking). Additionally, fluorocarbon polymer can be seeded into the pore structure of porous OSG films, magnifying the effect. We have previously examined this effect on planar samples in a conventional plasma etcher. However, the role of fluorocarbon polymerization on sidewall roughening/striation of OSG/porous OSG has not been investigated. Therefore, we have undertaken an examination of this sidewall roughening using a new, inductively coupled plasma beam source. This source allows the exposure of a sample to a realistic ion and neutral flux, of any desired plasma chemistry, while allowing independent control of the ion bombardment energy and incident angle. By rotating the sample to a near-glancing angle, a sidewall can be simulated, eliminating any effects associated with patterning. The effects of ion bombardment, impingement angle, and fluorocarbon chemistry (highly polymerizing vs. low polymerizing) on the roughening of SiO2, OSG, and porous OSG are discussed. Finally, insight into the surface roughening mechanism is obtained through modeling.

9:40am **PS1-MoM5 The Effects of Pore Morphology on the Diffusive Properties of a Porous Low-K Dielectric*, E.A. Joseph*,** *M.J. Goeckner, L.J. Overzet,* University of Texas at Dallas*; D.W. Gidley,* University of Michigan*; B.E.E. Kastenmeier,* IBM/International Sematech

Porous methylsilsesquioxane-based spin-on films with pore sizes of 1.5 - 2 nm and porosities ranging from 0 - 31% have been exposed to fluorocarbon and oxygen plasma chemistries to determine the integratability of the films. Using both spectroscopic ellipsometry and Auger electron spectroscopy, the porosity of the modified films was found to decrease during fluorocarbon and oxygen plasma exposure due to fluorine in-diffusion and carbon depletion, respectively. The depth of these compositional modifications is also measured and correlated to the porosity and pore interconnectivity, determined from Positronium Annihilation Lifetime Spectroscopy. Parallel studies of TaN atomic layer deposition also reveal tantalum in-diffusion, with diffusion lengths ranging from 40 - 125 nm (depending on porosity), and are comparable to those of fluorine, indicating that the diffusion and depletion lengths are governed by pore size and interconnectivity and are not material dependent. Lastly, moisture uptake in these films was examined and found to significantly affect both the overall porosity of the unprocessed films as well as the diffusion and depletion lengths of fluorine and carbon. @FootnoteText@ This work is supported by a grant from NSF/DOE, CTS-0078669.

10:00am **PS1-MoM6 Using In-vacuo Electron-Spin-Resonance and Infrared Spectroscopy Technique in the Analysis of Surface Reactions of Low-k films during/after Plasma Processes*, K. Ishikawa*,** Tohoku University, Japan*; Y. Yamazaki, S. Yamasaki,* AIST, Japan*; T. Ozaki, Y. Ishikawa, S. Noda, S. Samukawa,* Tohoku University, Japan

Using in-vacuo electron-spin-resonance (ESR) and infrared spectroscopy (FT-IR) techniques, surface reactions of low-k (porous methylsilsesquioxane, MSQ) films during/after plasma processes were studied. To understand the reaction mechanism on the surface with impinging species as ions, radicals, and photons, creation of dangling bonds (DBs), namely, bond breaking, is indeed a key process. The created DBs are playing an important role for surface chemical reactions. Applying our knowledge about pure SiO@sub 2@, the extensive study was made with respect to the porous MSQ, which is a candidate for future 45 nm node devices. Samples were prepared by spin-on coating a film of porous MSQ, on a bare Si substrate. The substrate was placed in a parallel-plate type reactor. Plasma discharge was sustained for proccessing. Since the DBs are affected by air exposure, our in-vacuo measurement needs to observe real feature of DBs. Thus, soon after the plasma process, an ESR spectrum was measured following transferring to the ESR cavity under vacuum ambient. Carbon-DB in the film is identifiable from g-value of the ESR signal. This indicates that the plasma process creates easily carbon-DBs, which has a highly chemical reactivity with oxygen.@footnote 1@ We also carried out an experiment using FT-IR. On an infrared spectrum of the film after the process, the decrease of the peak arising from Si-CH@sub 3@ bonds was clearly observed. Tentatively, we speculate that not only reactive species but also plasma characteristics as emissions affects to creation of the carbon-DBs and the created C-DBs plays an important role for the surface modification during/after the plasma process. @FootnoteText@ @footnote 1@ K. Ishikawa, et al. Appl. Phys. Lett. 81, 1773 (2002).

10:20am **PS1-MoM7 Minimizing low-k Damage during In-situ Photoresist Strip*, E.A. Hudson*,** *T. Choi, O. Turmel, L. Zheng, K. Takeshita, S. Lee, P. Cirigliano,* Lam Research Corp.

To increase the speed of devices, microelectronics fabrication is shifting to low-k dielectric materials as insulators for interconnect layers. k values may be reduced below ~3.0 using carbon-doped materials such as organosilicate glass (OSG). k is further reduced, below ~2.5, by introducing pores in the film. Problems may arise, however, because carbon is easily removed from these materials during plasma processing, specifically during the etching of lines and vias, and the photoresist strip after etch. Carbon loss causes an increase in the dielectric constant and thus degrades device performance. This paper focuses on the damage trends for carbon-doped dielectrics arising from in-situ photoresist strip in a capacitively-coupled dielectric etch system. Microscopic test structures have been developed, which allow direct measurement of the intrinsic damage which results from the interaction of the plasma strip environment with the unprotected and unmodified sidewall of a trench. Damage trends have been evaluated as a function of pressure and frequency of RF excitation during the strip. Damage is minimized for pressures in the 10 - 50 mTorr range. Etch processes typically leave a polymer coating on the sidewall of trenches and vias. This sidewall passivation is found to greatly reduce the low-k damage induced by the strip process. Ultimately the polymer must be removed from the sidewall to allow subsequent fabrication steps, but during the strip this film acts as a protective barrier against low-k damage. Therefore an overall strategy for minimizing damage is to run a low pressure strip, under conditions which preserve sidewall passivation as long as possible.

10:40am **PS1-MoM8 Comparison of In-situ and Ex-situ Resist Strip Process for Ultra Low-k/ Cu Interconnect*, H. Xu*,** *A. Shen, V. Tarasov,* ULVAC Technologies*; B. White, J. Wolf,* International Sematech

According to the ITRS roadmap, ILD layer with effective dielectric constant (k@sub eff@) of < 2.7 will be needed for 65 um technology node for high performance logic devices. To achieve k@sub eff@ of < 2.7, ultra low-k film with bulk k of < 2.1 will be needed. One of the challenges in integrating the ultra low-k material is the susceptibility of low-k material to damage from the post etch resist ashing and residue clean process. Directional resist ashing at low wafer temperature may provide a solution for avoiding damage to ultra low-k materials. Directional resist ashing can be done either in situ in a low-k etch chamber or ex situ in a standalone ash chamber. In this paper we will compare the process results between in situ and ex situ resist ash for ultra low-k film. The N@sub 2@/H@sub 2@ in situ ashing was done in a low k etch chamber which is a magnetically enhanced RIE reactor. The O@sub 2@ based ex situ ashing was done in a plasma chamber on an asher platform. This chamber incorporates a WCP plasma source and an independent wafer RF bias for independent plasma density and ion energy control. The WCP source was an ULVAC designed inductively coupled plasma source for achieving higher plasma density and lower electron temperature than a conventional ICP source. One experiment with an N@sub 2@/H@sub 2@ chemistry shows that while both in situ and ex situ resist ash shows comparable RC products. The RC product is an indirect measure of k@sub eff@, obtained from serpentine and comb test structure of 0.125/0.175um line width/spacing, indicating equally low damage to the ultra low-k film by the ash process. The ex situ N@sub 2@/H@sub 2@ ash process caused much less corner rounding of the SiC cap layer . Another experiment using a dilute O@sub 2@ ash process, shows that the RC product is sensitive to the chamber conditions used for resist ashing, suggesting mixing low k etch with O@sub 2@ based resist ash in the same chamber may cause more damage to ultra low-k film.

11:00am **PS1-MoM9 Impact of Different Ashing Plasmas on Porous and Dense SiOCH***, **T. Chevolleau,*** LTM-CNRS, France*; N. Posseme,* STMicroelectronics, France*; T. David, O. Joubert,* CNRS/LTM, France*; O. Louveau,* STMicroelectronics, France*; D. Louis,* CEA-LETI, France

In CMOS technology, the introduction of porosity into Low-k dielectric is the dominant strategy to achieve future generation of ultra low K interlayer dielectric materials (k~2.2). One of the integration challenges with these new materials are their structural modification during the etch and stripping processes due to a higher sensitivity with respect to the plasma . This study is dedicated to the impact of ash processes on a non porous SiOCH (k = 2.9) and a porous SiOCH (k=2.2, 50% void). The ash processes were carried out on blanket wafers either in a Magnetically Enhanced Reactive Ion Etcher using O@sub2@ and NH@sub3@ plasmas or in a photoresist stripper using H@sub2@ and O@sub2@ based downstream microwave plasmas. After plasma exposure, the surface and bulk modification of SiOCH films are investigated using quasi in-situ X-Ray Photoelectron Spectroscopy, Attenuated Total Reflection spectroscopy, Spectroscopic Ellipsometry and contact angle. The results show that the degree of SiOCH bulk modification is related to the carbon depletion and the moisture adsorption in the remaining film after plasma exposure. The materials are not altered in an H@sub2@ based plasmas without nitrogen whereas a film degradation is clearly pointed out in O@sub2@ based plasmas. When N@sub2@ is added to O@sub2@ or H@sub2@ plasmas, the porous film degradation is significantly enhanced. These results reveal that the best ash chemistries are H@sub2@/Ar and H@sub2@/He gas mixture. The P.R stripping feasibility on porous SiOCH films integrated in a single damascene structure is also performed and electrical results demonstrate that NH@sub3@ and H@sub2@/He ashing chemistries minimize the degradation of porous SiOCH compared to oxygen containing gas mixtures. Furthermore, Energy Filtred Transmission Electron Microscopy analyses reveal an efficient pore sealing with the NH@sub3@ chemistry leading to the elimination of TiN diffusion through the pores during barrier deposition.

11:20am **PS1-MoM10 Analysis of Ash-Induced Modification of Porous Organosilicate Glass Inter-Level Dielectric Materials on Patterned Structures Utilizing Electron Energy Loss Spectroscopy and Angular Resolved XPS***, **N.C.M. Fuller**, T.J. Dalton,* IBM TJ Watson Research Center*; C. Labelle,* Advanced Micro Devices Inc.*; M.A. Worsley,* IBM TJ Watson Research Center, Stanford University*; D. Dunn, T.S.L. Tai,* IBM Microelectronics Division

We have previously illustrated the need for analyzing patterned structures versus blanket wafers to effectively understand the dominant mechanism(s) effecting inter-level dielectric (ILD) modification during photoresist removal for damascene processing. The evolution of CMOS technology to maintain the ITRS roadmap potentially demands the introduction of porous (OSG or SiCOH)-based materials which are even more susceptible to ash-induced modification than their dense counterparts; as a consequence, the demand not only for finding a suitable ash solution (for specific integration schemes), but also for completely understanding the dominant mechanism(s) that modify these porous films is quite critical. Work to date by these authors has concentrated on analyzing ash-exposed ILD surfaces via electron energy loss spectroscopy (EELS) and examining the chemical changes in the surface as a function of ash chemistry/conditions. This work will summarize recent efforts aimed at further unraveling the mechanism(s) that influence the modification of relevant porous OSG-based ILD materials via the use of both EELS and the more sensitive angular resolved XPS (AR XPS) on both 200mm and 300mm patterned wafers. Relevant results will be presented.

11:40am **PS1-MoM11 Highly Selective Etching of Si@sub 3@N@sub 4@ to SiOC by Precise Ion Energy Control for sub-90 nm Dual Damascene Formation***, **H. Hayashi**, A. Kojima, A. Takase, K. Yamamoto, I. Sakai, T. Ohiwa,* Toshiba Corporation, Japan

Sub-90nm LSIs designed for high speed and low power operations, demand introduction of low-k material for interlayer dielectric material. We have reported that the 100 MHz rf capacitive coupled plasma (CCP) RIE process is the most suitable for etching organic film because of its low ion energy@footnote 1@@super ,@@footnote 2@. Furthermore, for low-k SiOC film etching which requires a higher energy etch process, we have developed dual frequency superimposed (DFS) 100 MHz and 3.2 MHz rf CCP etch processes, which can control electron density and self-bias voltage independently in a wide range. In the damascene etch process of SiOC film using Si@sub 3@N@sub 4@ as etch mask, it was observed that the mask edge erosion is strongly dependent on ion energy regardless of selectivity. An excellent etch profile, as well as selectivity was realized by precise ion energy control@footnote 3@. We have newly developed a highly selective Si@sub 3@N@sub 4@ to SiOC etch process with CF@sub 4@/H@sub 2@ gas chemistry, which requires the reverse selectivity. Such a selective etch process enables dual damascene interconnects formation with a much lower dielectric constant. The blanket SiOC etch rate decreased as H@sub 2@ addition to CF@sub 4@ was increased, and became zero when the H@sub 2@ flow rate was equal to the CF@sub 4@ flow rate. The blanket Si@sub 3@N@sub 4@ etch rate did not decrease with H@sub 2@ addition, so high selectivity was achieved, regardless of ion energy. Next, this highly selective process condition was applied to Si@sub 3@N@sub 4@ etching using SiOC mask, where again, mask edge erosion was dependent on ion energy regardless of selectivity. Highly selective damascene etching of Si@sub 3@N@sub 4@ was realized by precise ion energy control using DFS RIE. @FootnoteText@ @footnote 1@H. Hayashi et. al., Symp. Dry. Process. (2002) p.195@footnote 2@H. Hayashi et. al., AVS 50th Symp. (2003) PS-TuA5@footnote 3@A. Kojima et. al., Symp. Dry. Process. (2003) p.13.

Plasma Science and Technology
Room 213B - Session PS2-MoM

Silicon Etching

Moderator: F. Celii, Texas Instruments

8:20am **PS2-MoM1 Challenges Facing Deep Trench Silicon Etching for Present and Future Trench Technology Nodes***, **A.M. Paterson**, S. Pamarthy, A. Khan, F. Ameri, J.Y. Chen, H. Mohiuddin, T. Panagopoulos, J.P. Holland, T. Lill,* Applied Materials, Inc.*; A. Steinbach, S. Wege,* Infineon Technologies

The reduction in trench technology nodes to 90nm and beyond brings new challenges to deep trench silicon etching of capacitor structures for DRAM applications. At present gate feature sizes of 110nm requires silicon trench etching depths of 8um, with a top critical dimension of 160nm, corresponding to an aspect ratio of 50:1. The depth, and hence aspect ratio of the trench, is determined by customer capacitor cell and leakage current requirements. In the next five years, the trench nodes will reduce further to 90nm, 70nm and 65nm with the aspect ratios of the silicon trench increasing to 65:1, 80:1 and 100:1, respectively. The shrinking of the node to smaller sizes brings new challenges to semiconductor OEMS. The technology that was used for etching trenches at one node size may not give the required trench at the smaller node size. This was found to be the case when moving from 0.35µm to 0.25µm node size where the tool of choice, AMAT DPS@super TM@ DT, had limitations in obtaining the required customer specifications for the new node. After subsequent research and development at Applied Materials, a new High Aspect Ratio Trench (HART@super TM@) chamber has shown the capability of etching trenches down to the 70nm node. This paper will discuss why the choice of plasma source, source rf frequency, bias rf frequency and chamber geometry are of critical importance in achieving such high aspect ratio trenches.

8:40am **PS2-MoM2 Etching High Aspect Ratio Structures in Si using SF@sub 6@/O@sub 2@ Plasma: Experiments and Feature Scale Modeling***, **R.J. Belen**[1], S. Gomez,* University of California Santa Barbara*; M. Kiehlbauch, D. Cooperberg,* Lam Research Corporation*; E.S. Aydil,* University of California Santa Barbara

Plasma etching of high aspect ratio structures in Si is an important step in the manufacture of memory devices and MEMS components. The goal is to etch deep features anisotropically with high etch rates, high selectivity to the mask and good uniformity. We have studied the etching of deep sub-micron diameter holes in Si using SF@sub 6@/O@sub 2@ plasma. Our approach is to combine experiments and plasma diagnostics with feature scale modeling to gain a fundamental understanding of the etching kinetics necessary to develop and scale-up processes. Etching experiments are conducted in a low pressure, high density, inductively coupled plasma etching reactor. Visualization of the profiles with SEM is used together with plasma diagnostics such as optical emission and mass spectroscopies to study the effect of pressure, rf-bias voltage and SF@sub 6@-to-O@sub 2@ gas ratio on the etch rate, selectivity and feature profile shape. Simultaneous with experiments, we have developed a feature scale model of the etching process. Information from plasma diagnostics and previously published data are used to reduce the degrees of freedom in the model by estimating F, O, and ion fluxes and ion energy and angle distributions. We have designed experiments to directly measure parameters such as the chemical etch rate constant and the etch yield dependence on the ion angle. Experimentally inaccessible parameters such as sticking coefficients and etch yields are determined by matching simulated profiles with those experimentally observed under various etching conditions. The F-to-ion flux ratio and F-to-O flux ratio are found to be the important plasma parameters that determine the etch rate and anisotropy. Plasma diagnostics provide quantitative information about the location of the ion and neutral-limited regimes in the operating parameter space. The SF@sub 6@-to-O@sub 2@ gas ratio determines the balance between etching and sidewall passivation, which controls the feature profile shape.

9:00am **PS2-MoM3 Etch Rate and Profile Evolution Model for High Aspect Ratio Etch in HBr/NF3/O2 Plasma***, **A. Kersch**, W. Jacobs, W. Sabisch, G. Schulze-Icking, A. Henke, S. Wege,* Infineon Technologies AG, Germany

Silicon etching based on a HBr/O2/NF3 plasma generated in a capacitively coupled Merie plasma reactor is used to fabricate DRAM trench capacitors. To maintain a constant capacitance per memory cell an optimum aspect ratio and trench shape with respect to capacitance and cost has to be achieved. In this paper we report about two feature scale models of different complexity. A compact model calculates the etch rate for a given trench geometry by solving an integral equation for the neutral and ion transport inside the trench. Input parameter are ion and fast neutral fluxes and their energy distribution as a function of CCP power, pressure, magnetic field, and the fluxes of reactive radicals as a function of plasma and gas flow conditions. The efficiency of this approach allows the investigation of effects of trench profile on the etch rate for a variety of data. A high level model calculates in addition the trench profile evolution as a function of the above parameters supplemented by the particles angular distribution, a surface scattering distribution, and a chemical rate model for etch and side wall passivation. These calculations are done with an axisymmetric/3D profile simulator (TOPSI3D) which used level set front propagation, Monte Carlo particle transport, and chemical surface reaction rates (1). For the selection of the input parameter, a combination of experimental values (plasma density, V-I measurement, RGA) and reactor scale simulation (plasma, neutral gas flow and collisional sheath) is used. The paper focuses on the effects of power, magnetic field, pressure and gas flow on the etch rate and trench profile. The results of both models are in good agreement with each other as well as with experimental data for several technology nodes. @FootnoteText@ @footnote 1@ W.Jacobs et al, IEDM Tech. Digest, Session 35/5, 2002 .

9:20am **PS2-MoM4 Optimal Chamber Aspect Ratio of an Inductively Coupled Plasma Etcher for Advanced Gate Application***, **Y.D. Du**,* Applied Materials Inc.

It has been known that the chamber aspect ratio (length/radius) played a significant role in defining ion flux and neutral flux uniformity (including passivaiton distribution) across the wafer in an inductively coupled plasma source. This paper will present a detailed study of silicon etch rate and CD uniformity as a function of chamber aspect ratio. Process parameters such as pressure, power and chemistry dependence on etch rate and CD uniformity are systematically compared under different chamber body length. A series of plasma modeling and gas flow modeling using a 2-D axisymmetrical fluid model are conducted and compared with the experimental data. The results show that an optimal chamber aspect ratio design requires careful balancing of plasma source uniformity as well as by-products distribution across the wafer in order to meet the overall stringent gate patterning etch requirements.

9:40am **PS2-MoM5 Highly Anisotropic and Damage-free Gate Electrode Patterning in Neutral Beam Etching Using F@sub 2@ Based Gas Chemistry***, **S. Noda**,* Tohoku University, Japan*; Y. Hoshino,* Showa Denko K.K., Japan*; T. Ozaki, S. Samukawa,* Tohoku University, Japan

Neutral beam etching is a promising candidate for the damage-free processing of semiconductor devices. To realize high-performance etching processes, we developed a new neutral beam etching system. In this system, highly efficient neutral beams could be obtained by accelerating negative ions generated in the pulse-time-modulated plasma. Damage-free 50 nm poly-Si gate electrode patterning has already been accomplished by our system using the Cl@sub 2@/SF@sub 6@ mixture gas chemistry@footnote 1@. In this gas chemistry, accelerated Cl and F atoms contributed to the etching reaction and the etching profiles were controlled by changing the gas flow ratio. However, the etching rate and the pattern profile were drastically varied with changing the gas flow ratio. Especially, by increasing the SF@sub 6@ flow rate, both the etching rate and the side etching increased rapidly. There were trade-off between the etching rate and etching profile in the SF@sub 6@ based gas chemistry. Namely, SF@sub 6@ plasma generated a large amount of F radicals. To settle this problem, F@sub 2@ gas plasma was investigated to generate the fast F atom beam efficiently with maintaining low density of F radical. In comparison between F@sub 2@ and SF@sub 6@, great differences were observed in the etching characteristics. Even in the case of pure F@sub 2@ gas chemistry, the etching anisotropy drastically increased and the side etching of poly-Si hardly occurred. It is caused by elimination of the F radical generation and increase of negative ion (F@super -@) generation in the F@sub 2@ plasma. Using this feature, more flexible and precise control will be achieved in the neutral beam etching method. @FootnoteText@ S. Noda et al., to be published in J. Vac. Sci. and Technol. A, Jul/Aug (2004).

10:00am **PS2-MoM6 Silicon Recess Formation During High Density Plasma Polysilicon Gate Etching***, **S.A. Vitale**, B.A. Smith,* Texas Instruments

Silicon loss during gate etch from the active region of a traditional CMOS transistor is shown to take place through plasma oxidation of the silicon substrate during the over-etch step. The plasma oxidation occurs by an ion-enhanced process with an activation energy of only 0.02 eV. This phenomenon is successfully modeled using the traditional Deal-Grove thermal oxidation model, with the inclusion of a depth-dependent reaction rate constant to incorporate the ion-enhancement effect. Plasma oxidation and silicon loss are reduced by using a shorter poly over-etch time, lower source and bias power, lower substrate temperature, and lower O2 flow. A viable poly-over etch process was developed which produced vertical poly profiles while reducing the silicon loss by 32%.

10:20am **PS2-MoM7 Deep Cryo-Etching for Silicon Structures***, **T.T. Tillocher**, R.D. Dussart, X.M. Mellhaoui, P.L. Lefaucheux,* GREMI - Orléans University, France*; M.B. Boufnichel,* ST Microelectronics - Tours, France*; P.R. Ranson,* GREMI - Orléans University, France

Semiconductor technology requires more and more accuracy in deep etching. The cryogenic process, which uses a SF@sub 6@/O@sub 2@-based chemistry and a cryogenically cooled wafer chuck, is promised to a great future since it provides smooth profiles and high etch rates. Indeed, this cryo-etching enables to realise with these good performances different patterns on silicon and SOI wafers (vias, trenches...) for a wide range of mask openings. This process is very accurate and fastidious to control since its efficiency results from a weak equilibrium between the simultaneous etching and passivation mechanisms. If the latter is broken, defects (black silicon, notching, bowing, undercut...) can appear and grow very quickly. We will detail these different defects and their conditions of appearance. A new cryogenic chuck, associating electrostatic clamping and a very good temperature uniformity , allows the etching of very uniform profiles all over the surface of the 6'' wafers. This is a critical aspect in the project since for certain projects the two sides of the wafer have to be etched separately and the profiles, depending on the temperature, must have the same shape from one side to the other. Parallel plasma diagnostics, such as

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

actinometry, Langmuir probe, FTIR, interferometry, are the key to a better understanding of the process and hence to better control the process. We will present our last results on projects carried out in collaboration with STMicroelectronics/Tours. Some plasma measurements will be presented and correlated to the etching performances.

11:00am **PS2-MoM9 Atomic-scale Simulations of Spontaneous and Ion-assisted Etching of Silicon***, **D. Humbird**, D.B. Graves,* University of California, Berkeley

Molecular dynamics (MD) simulations model the phenomenon of thermal halogen atoms etching silicon spontaneously, and capture the atomic-scale mechanisms of Ar@super +@ ions and neutral halogen atoms working together. Using improved interatomic potential energy functions for Si-F and Si-Cl, MD predicts steady halogen uptake and spontaneous etching as F and Cl atoms impact Si. At 300 K, the simulations agree semi-quantitatively with experimental measurements of total surface coverage, halosilyl group coverage, reaction probability, and etch product distribution. Etch products that remain weakly bound to the surface are detected in significant quantities. At higher temperature, agreement between simulation and experiment is qualitative; the simulation matches trends in reaction probability and etch product redistribution. Below 450 K, etch products form and promptly desorb. At higher temperatures, internal decomposition of the halogenated silicon layer dominates. The forthcoming phenomenological model of Winters et al. is based in part on some of the observations of our simulations@footnote 1@. Significant etching enhancements are realized when simultaneous energetic Ar@super +@ ions impact the halogenated Si surface. Si etch yields are in good agreement with experiments. The atomic-scale mechanisms of ion-enhanced etching are classified as enhanced spontaneous etching, chemically enhanced physical sputtering, and chemical sputtering. The primary effects of ions are to increase the local surface coverage of etchant species and to create products by inducing chemical reactions within the halogenated surface layer. Ion-assisted effects are most pronounced at low neutral/ion ratio and decline as this ratio increases. Explicit ion enhancements are greater for Cl than for F. @FootnoteText@ @footnote 1@HF Winters, D Humbird, and DB Graves, in preparation (2004).

11:20am **PS2-MoM10 X-ray Photoelectron Spectroscopy Analyses of SiGe and Si Surfaces after Selective Etching of Si***, **S. Borel**, O. Renault, J. Bilde,* CEA-DRT-LETI, France

Recent progress in thin films epitaxial growth enables to consider new applications based on the realisation of Si/SiGe/Si heterostuctures. Indeed, lateral etching process can removed either SiGe or Si sacrificial layer and leads to a cavity between two single crystal-layers. The empty space thus created can be filled by an amorphous material in order to obtain a mono-layer on a insulator (Silicon On Nothing transistors). The selectivity of such processes is crucial for safeguarding of transistors actives parts dimensions. The Si removal etching process is as much more interesting because the selectivity to SiGe is almost infinite. The infinitely selective isotropic etching of Si to SiGe@footnote 1@, obtained by using a combined addition of N@sub 2@ and CH@sub 2@F@sub 2@ into O@sub 2@ +CF@sub 4@ plasma was studied by ex-situ X-ray photoelectron spectroscopy. Etched Si and SiGe surfaces were analysed in terms of elemental composition, bonding states and oxide/oxyfluoride thickness by careful decomposition of Ge3d, Si2p, C1s and F1s core-level spectra. Both F1s and C1s spectra show up a component due to fluorocarbon polymeric groups, the quantity of which is 3 times higher on SiGe than on Si. At the same time on SiGe surfaces, F1s and Ge3d spectra reveal a large formation of Ge(O@sub x@)F@sub y@ bonds compared to metallic Ge, whereas SiF@sub x@ are almost absent. We conclude that a layer formed by a fluorocarbon polymer and Ge oxyfloride induces a total passivation of the SiGe when subjected to the N@sub 2@ /CH@sub 2@F@sub 2@/O@sub 2@+CF@sub 4@ plasma. The precise role of the CH@sub 2@F@sub 2@ will be tentatively interpreted on the basis of other etching results with similar inverted selectivities. @FootnoteText@ @footnote 1@ S. Borel et al., Jpn. J. Appl. Phys. (accepted).

Semiconductors

Room 304B - Session SC+MI-MoM

Dilute Magnetic and Ferromagnetic Semiconductors

Moderator: C.J. Palmström, University of Minnesota

8:20am **SC+MI-MoM1 Heterointerfaces and Magnetism in Ferromagnetic Semiconductor Heterostructures***, **N. Samarth**,* Pennsylvania State University **INVITED**

We discuss recent experiments that demonstrate how heterointerfaces impact the magnetic properties of heterostructures derived from the "canonical" ferromagnetic semiconductor (Ga,Mn)As. In this material, holes created by the Mn acceptors mediate a ferromagnetic interaction between the Mn ions themselves, and the Curie temperature is determined by a complex interplay between substitutional magnetic ions, interstitial defects and holes. Although as grown epilayers of (Ga,Mn)As typically have Curie temperatures lower than 110 K, post-growth annealing at low temperatures (180 C - 250 C) significantly enhances the ferromagnetic properties, leading to Curie temperatures above 150 K. The first set of experiments examines the effects of capping ferromagnetic Ga1-xMnxAs epilayers with a thin layer of undoped GaAs. We find that the overgrowth of even a few monolayers of GaAs significantly suppresses the enhancement of the ferromagnetism associated with low temperature annealing, suggesting that heterointerfaces have a direct impact on the migration of interstitial defects during post-growth annealing. In the next set of experiments, we demonstrate the first exchange biasing of (Ga,Mn)As by an overgrown antiferromagnet (MnO). Although the exchange bias effect is unambiguous when successful, we also find that the high reactivity between Mn and GaAs affects the ferromagnet/antiferromagnet heterointerface, presenting interesting experimental challenges for the routine achievement of exchange bias in this important spintronic material. This work was carried out in collaboration with K. C. Ku, M. B. Stone, K. F. Eid, P. Schiffer, T. Shih, and C. Palmstrom. Supported by ONR and DARPA.

9:00am **SC+MI-MoM3 Structural and Magnetic Properties of a Magnetic Semiconductor MnGeN@sub2@ Grown by MBE***, S.H. Cheung, M.L. Harland, V.K. Lazarov,* University of Wisconsin, Milwaukee*; Y. Zhang,* Peking University, China*; M. Weinert, M. Gajdardziska-Josifovska,* University of Wisconsin, Milwaukee*; Z. Gai,* Peking University, China*; **L. Li**,* University of Wisconsin, Milwaukee

A novel magnetic semiconductor MnGeN@sub2@ was synthesized on 6H-SiC(0001), Al@sub2@O@sub3@(0001), and MgO(111) substrates by plasma assisted molecular beam epitaxy. In situ reflection high-energy diffraction, ex situ atomic force microscopy and transmission electron microscopy (TEM) investigations indicate that the films grown are epitaxial on all three substrates, with the ones on MgO having the best overall quality. Detailed analysis of high-resolution TEM digital diffractograms and convergent beam electron diffraction patterns of the films show that the MnGeN@sub2@ is orthorhombic, and has the following crystallographic orientation relationships with the substrate: MnGeN@sub2@(001)//MgO(111), MnGeN@sub2@(100)//MgO(11-1), and MnGeN@sub2@(210)//MgO(01-1). Investigations by SQUID magnetometry indicate that the magnetic properties of the films can be controlled by the stoichiometry, i.e. Mn/Ge ratio, varying from paramagnetic to ferromagnetic, with the ferromagnetic samples exhibiting a Curie temperature above 300 K.

9:20am **SC+MI-MoM4 Thermal Stability of GaCrN Epitaxial Layers***, **G.T. Thaler**, R.M. Frazier, C.R. Abernathy, S.J. Pearton,* University of Florida

A number of recent studies have reported the observation of room temperature ferromagnetism in GaMnN. However, this material appears to be thermally unstable during processing at temperatures as low as 500°C unless co-doped with oxygen. For the development of spintronics devices based on GaN, thermal annealing at or above ~700°C is necessary to improve contact resistances and for p-dopant activation. An alternative material that has received some interest of late is GaCrN, which has also been reported to be ferromagnetic at room temperature. However, little is known as yet about the thermal stability of this material and its suitability for integration with GaN device processing technology. In this talk we will discuss the thermal stability of GaCrN and the effect of Cr concentration on both the as-grown magnetic behavior and the magnetic properties as a function of annealing. Epitaxial growth was performed using Gas Source Molecular Beam Epitaxy. Films with magnetic transition temperatures above room temperature were produced for a variety of Cr concentrations, though the signal appeared to maximize around 2-3% Cr, as is the case for

GaMnN. Unlike GaMnN, the addition of Cr to GaN produced material that was thermally stable after annealing up to 700°C with little change observed in the magnetic behavior of the GaCrN films. The implications of this stability for device processing and performance will also be discussed. This work was supported by the Army Research office under: ARO-DAAD19-01-1-0701 and by NSF under: ECS-0224203.

9:40am **SC+MI-MoM5 Structural Characterization of GaMnN Thin Films Grown by Chemical Beam Epitaxy (CBE).**, ***L.A. Carreno**, C. Boney, A. Bensaoula, Z. Zhang,* University of Houston

Diluted magnetic semiconductors (DMS) based on Mn doped GaN are intensively investigated for their potential spintronics applications. Ferromagnetism has been demonstrated in Mn-doped implanted p-type GaN, Mn-diffused GaN, and n-type films of GaMnN grown by MBE. Two approaches to understanding the magnetic properties of DMS materials are pursued: one considers these materials as more-or-less random alloys; the second one considers the magnetic atoms forming small clusters that produce the observed ferromagnetism. To clarify these issues we have performed structural analysis of GaMnN thin films grown by CBE using two in-situ time of flight (TOF) ion spectroscopy techniques combined with SARIC trajectory simulations. These were complemented with ex-situ XRD, PL, Raman spectroscopy, and Backscattering/ channeling combined with PIXE. GaMnN has been grown using TEG, NH@sub 3@, and solid Mn on sapphire/GaN templates prepared by CBE and MBE. Evolution of the stress for the as grown and annealed thin films has been studied by XRD and Raman. Samples grown on sapphire/GaN templates prepared by CBE show n-type conductivity, those grown on MBE GaN templates are highly resistive. The reactor is fitted with two in-situ TOF techniques, Direct Recoil Spectroscopy (DRS) and Mass Spectroscopy of Recoiled Ions. For structural characterization, azimuthal DRS scans are used to extract the surface periodicity and from that construct models of GaMnN surfaces. Simulations of scattering and recoiling scans for GaMnN surfaces have been performed for different possible lattice locations of Mn in GaN. Similar experiments were performed using Rutherford backscattering/channeling combined with particle induced X-ray emission. DRS confirmed retention of wurtzite crystal structure obtained by RHEED and XRD for Mn concentrations up to 2.5%. Although results have shown mainly substitutional incorporation of Mn atoms at Ga sites, DRS scans also show presence of Mn atoms at interstitial positions.

10:00am **SC+MI-MoM6 Induced Host Moments and Mn Electronic Structure in Mn-Doped Iii-V Ferromagnetic Semiconductors**, ***D.J. Keavney**,* Argonne National Laboratory*; D. Wu, J. Shi,* University of Utah*; E. Johnston-Halperin, D.D. Awschalom,* University of California, Santa Barbara*; Y. Cui, L. Li,* University of Wisconsin-Milwaukee **INVITED**

We have used soft x-ray magnetic circular dichroism (XMCD) and absorption spectroscopy (XAS) to examine induced host magnetic moments and the local Mn environment in Mn-doped GaAs and GaN. X-ray absorption probes unoccupied states via transitions from deep core levels, thus providing electronic structure information with element specificity. With circularly polarized radiation at the L edges, element specific moments can be detected via their projection onto the Mn 3d and host 4s states, providing a test of predictions made by the carrier-mediated model of ordering. In (Ga,Mn)As, we find small XMCD signals at the onset of the absorption edge for both Ga and As, which we attribute to induced 4s moments. The relative orientations of all three elements are as expected for carrier-mediated coupling, and we estimate that the As moment is larger than the Ga moment. In (Ga,Mn)N, we detect a weak Ga XMCD signal 2-3 eV above the absorption edge of opposite sign to that in (Ga,Mn)As, which may be attributable to Mn 3d tails at the Ga sites. The absence of a Ga 4s moment would suggest a weaker p-d hybridization consistent with the deeper position of the Mn acceptor level. In both systems, XAS shows that Mn is divalent, although with differing amounts of line broadening, suggesting that the Mn 3d localization varies significantly depending on the host. (Ga,Mn)N has a lineshape closer to atomic Mn 2+ than (Ga,Mn)As. These results show that the Mn 3d and valence band electronic structure in doped III-V systems is strongly dependent on the host, and have implications for the degree of p-d hybridization and the coupling mechanism responsible for ferromagnetism. Use of the Advanced Photon Source was supported by the U.S. DOE, Office of Science, Contract No. W-31-109-Eng-38. Work at the Univ. of Utah was supported by ONR/DARPA grant No. N00014-02-10595, at UCSB by ONR/DARPA grant No. N00014-99-1-1096 and AFOSR F49620-02-10036, and at Univ. of Wisconsin by NSF DMR-0094105.

10:40am **SC+MI-MoM8 Intrinsic Versus Extrinsic Nature of Co Doped TiO@sub 2@ Diluted Magnetic Semiconductor Thin Films**, ***S.R. Shinde**, S.B. Ogale, J. Higgins, T. Zhao,* University of Maryland*; S.E. Lofland,* Rowan University*; V.N. Kulkarni,* University of Maryland*; A.J. Millis,* Columbia University*; S. Das Sarma, R.L. Greene, R. Ramesh, T. Venkatesan,* University of Maryland

The issue of Co distribution in TiO@sub 2@ (in anatase and rutile forms), a widely studied oxide based diluted magnetic semiconductor (DMS) system, is still controversial. Although all the reported studies have discovered room temperature ferromagnetism in this system, some of the researchers claim that the material is intrinsic, whereas others have found that cobalt forms small clusters and therefore the material has extrinsic origin of ferromagnetism. In our work we have grown (by pulsed laser deposition) and characterized epitaxial thin films of Co:TiO@sub 2@ at different growth conditions and Co doping concentrations. We noticed that Co distribution strongly depends on the growth parameters. At lower growth temperature (~700C) there is a limited solubility of Co (up to ~2%) above which nanometer sized Co clusters are formed. When the films are grown in ultrahigh vacuum (10-8 Torr), the films have low resistivity and show the anomalous Hall effect. Although this could be interpreted as a signature of carrier induced DMS nature of these particular films, our detailed magnetic and structural analysis shows the presence of Co nanoclusters in these films. In the magnetization data of these films we observe superparamagnetism with a blocking temperature of 250K. This temperature corresponds to Co particles of 7nm diameter, the presence of which was further confirmed by transmission electron microscopy (TEM). On the other hand, when the films grown at lower temperature are annealed at high temperature (~900C) the clusters dissolve in titanium dioxide matrix leading to an intrinsic DMS with a Curie temperature ~650C. Similar properties are observed for films directly grown at high temperature and no indication of any clustering of Co is observed in TEM. We have also observed electric field induced reversible modulations, in the magnetization of these films in PbZr@sub 0.2@Ti@sub 0.8@O@sub 3@/Co:TiO@sub 2@/SrRuO@sub 3@ field effect transistor structure.

11:00am **SC+MI-MoM9 Ferroelectric Field Effect on Ferromagnetism in Diluted Magnetic Insulator Anatase Co:TiO@sub2@**, ***T. Zhao**, S.R. Shinde, S.B. Ogale, H. Zheng, T. Venkatesan,* University of Maryland*; R. Ramesh,* University of California, Berkeley*; S. Das Sarma,* University of Maryland*; J. Misewich,* Brookhaven National Laboratory

Recently considerable success is reported in making a non-magnetic semiconductor ferromagnetic by dilute doping of magnetic impurities. However, the possibilities of extrinsic effects such as dopant clustering, impurity magnetic phases etc., have not been completely ruled out in many systems. In this work we report the first successful implementation of an external electric field modulation of ferromagnetism in an oxide-based DMS anatase Co:TiO@sub2@. An anatase TiO2 layer with 7% Co doping and a ferroelectric PbZr@sub0.2@Ti@sub0.8@O@sub3@ layer were epitaxially grown on a conducting SrRuO@sub3@ buffered LaAlO@sub3@ substrate by pulsed laser deposition. The high-quality of epitaxy and uniform distribution of Co were confirmed by X-Ray diffraction and transmission electron microcopy. The Co:TiO@sub2@ channel grown in this case at a high temperature of 875°C is insulating in nature. The magnetic hysteresis loops of the Co:TiO@sub2@ were measured by superconducting quantum interference device after positive or negative electric poling on PZT. The room temperature saturated magnetic moment clearly shows two stable states which are reversible by switching the ferroelectric polarization. The observed effect, which is about 15% in strength can be modulated over several cycles. This first demonstration of electric field effect in an oxide based diluted ferromagnetic insulator system provides evidence of its intrinsic nature. Furthermore, the ability of electric field modulation of ferromagnetism is very promising for next-generation multi-functional electronic devices. Possible mechanisms for electric field induced modulation of insulating ferromagnetism are discussed. This work was supported by DARPA SpinS program (through US-ONR) and the NSF-MRSEC (DMR 00-80008) at Maryland. The PLD and RBS facilities used in this work are shared experimental facilities (SEF) supported in part under NSF-MRSEC.

11:20am **SC+MI-MoM10 Applications of a Dilute Magnetic Semiconductor Based on AlN**, ***R.M. Frazier**, G.T. Thaler, J.Y. Leifer, C.R. Abernathy, S.J. Pearton,* University of Florida

With the increasing interest in spintronics, many attempts have been made at incorporating spin-based functionality into existing semiconductor technology. One approach, utilizing dilute magnetic semiconductors (DMS) formed via introduction of transition metal ions into III-Nitride hosts, would allow for integration of spin based phenomena into current wide bandgap technology. Further, the use of AlN broadens III-V DMS applications to tunneling devices and UV light emitters. The most evident application of ferromagnetic AlN is as a ferromagnetic tunnel barrier, similar to EuS, but unlike EuS should allow for operation at room temperature. Ion implantation has been shown to be an effective survey method for introduction of various transition metals into AlN. However, it is not a technique which will allow for the development of advanced spin based devices. Such devices will require epitaxial methods of the sort currently used for synthesis of III-Nitride optoelectronics. In this study, one such technique, Gas Source Molecular Beam Epitaxy (GSMBE) has been used to synthesize AlN films doped with Cr and Mn. In the Mn doped films, increasing the V/III ratio corresponded to an increased magnetic signal, indicating an increase in active Mn sites. In the case of both Mn and Cr doped AlN, the magnetic signal was found to depend on the flux of the dopant, and the optimal growth conditions were found. Growth of tunnel devices using AlTMN as a barrier will also be discussed. This work is supported by the Army Research Office under ARO-DAAD19-01-0-0701 and NSF under ECS-0224203.

11:40am **SC+MI-MoM11 Ferromagnetism and Polaron Percolation in Mn@sub x@Ge@sub 1-x@ Dilute Magnetic Semiconductor***, **A.P. Li**, J.F. Wendelken, J. Shen,* Oak Ridge National Laboratory*; J.R. Thompson, H.H. Weitering,* Oak Ridge National Laboratory, University of Tennessee

In dilute magnetic semiconductors (DMS), ferromagnetic ordering is carrier mediated. This picture seems to be accepted more or less universally, but the detailed nature of the ferromagnetism varies greatly from system to system. We have studied ferromagnetism and the correlation between transport and ferromagnetism in Mn@sub x@Ge@sub 1-x@ DMS for Mn concentrations up to 9%. By carefully controlling the growth conditions, we obtained precipitate-free Mn@sub x@Ge@sub 1-x@ that exhibits magnetic phase transitions at Tc = 20 K and Tc* = 112 K. The magnetic response to temperature and doping concentration is indicative of a magnetic-polaron percolation transition at Tc [1], which coincides with a metal-insulator transition and Hall-effect sign anomaly. Tc* is the ferromagnetic ordering temperature within isolated polarons which can be determined from a Curie-Weiss plot of the high-temperature magnetic susceptibility. Ferromagnetism in Mn@sub x@Ge@sub 1-x@ DMS reveals a striking analogy with the magnetism of so-called "clustered states" in manganite compounds [2]. [1] A. Kaminski and S. Das Sarma, Phys. Rev. B 68, 235210 (2003) [2] G. Alvarez and E. Dagotto, Phys. Rev. B 68, 045202 (2003).

Advanced Surface Engineering
Room 303D - Session SE-MoM

Nanolayered and Gradient Coatings for Surface Engineering

Moderator: A.A. Voevodin, Air Force Research Laboratory

8:20am **SE-MoM1 Structure and Hardening in TiN/a-SiNx Multilayers and Self Organizing Ti1-xAlxN Films***, **M. Oden**,* Lulea University of Technology, Sweden **INVITED**

This talk will cover two distinctly different mechanically hard films. The first is a dual reactive magnetron sputtered mulilayer consisting of alternating polycrystalline TiN and amorphous SiNx layers. The TiN layers exhibit a preferred 200 orientation for layer thicknesses below 10 nm. For thicker layers 111 orientations are also observed. The amorphous SiNx layers provides for TiN renulcleation in each layer yielding a column free microstructure. Nanoindentation was used to evaluate the hardness which varied between 18 to 32 GPa depending on the layer modulation. For large wavelength (>20 nm), Hall-Petch dependence is observed with a generalized power of -0.4. For shorter wavelengths superhardening yields a deviation from the Hall-Petch relationship. The highest hardness is observed for mulilayers having thin SiNx -layers (< 1nm) for which HRTEM reveals a transformation from amorphous to crystalline SiNx layers growing cube on cube on the TiN crystals. The formation of crystalline SiNx and its influence on hardening is discussed. The second material system to be reviewed is arc evaporated Ti1-xAlxN with a range of compositions (x=0 to 0.74). As-deposited coatings with xï,£0.66 had metastable cubic structures. Annealing at 1100 Â°C of these films resulted in phase separation of c-TiN and h-AlN, via spinodal decomposition of c-TiN and c-AlN. The high hardness (~37 GPa) and texture of the Ti1-xAlxN coatings are retained for annealing temperatures up to 950ï,°C, which indicates a superior stability of this system compared to TiN and Ti(C,N) coatings. It is proposed that competing mechanisms are responsible for the effectively constant hardness; softening by lattice defect annihilation is balanced by hardening from formation of a nano-composite structure of c-AlN volumes by spinodal decomposition.

9:00am **SE-MoM3 Structure and Optical Behavior of As-Grown and Annealed Titania/Alumina Nanolaminate Films***, **M.A. Omari**, R.S. Sorbello, C.R. Aita,* University of Wisconsin-Milwaukee

Titania-alumina nanocomposites are of current interest for optical, catalytic, and sensor applications. A wide range of desirable properties can be obtained by varying the amount of each constituent. A convenient way of incorporating tailored nanocomposites in thin film structures is by using a nanolaminate structure. We report here the fabrication, structure, and optical behavior of titania-alumina nanolaminates. 150 nm-thick multilayer films were grown at room temperature on silica substrates by sequential reactive sputtering of metal targets in argon/20% oxygen rf discharges. The nominal titania layer thickness was varied from 1.25 to 45 nm, and the alumina layer thickness was kept constant at 5 nm. X-ray diffraction and spectrophotometry were used for film analysis. The films were cyclically annealed at 700 and 1000 deg. C from 15 min to 10 h. Alumina was amorphous in as-grown and annealed films. Titania in as-grown films consisted of rutile nanocrystals embedded in an amorphous matrix. No anatase was present, nor was anatase formed by annealing. High temperature annealing produced a series of crystalline (Ti,Al)-oxide interface phases. Optical band gap and refractive index measurements indicate that significant interfacial mixing occurred in as-grown films, as well.

9:20am **SE-MoM4 The Growth of Depth-Graded WSi@sub 2@/Si Multilayer Linear Zone Plates****, **C. Liu**, R. Conley, A.T. Macrander, J. Maser, H.C. Kang, G.B. Stephenson,* Argonne National Laboratory

Fresnel zone plates, consisting of alternating transparent and opaque rings designed according to Fresnel phase conditions, are widely used to focus x-rays. Zone plates are commonly made using lithographic techniques and have achieved high spatial resolution on the order of 20 nm in the soft x-ray range. For hard x-rays, to achieve an optimum efficiency, the thickness of the zone plate needs to be several microns. The required high aspect ratio is difficult for lithography and imposes a limit to the focus spot size. Techniques have been developed using sectioned multilayer-coated wires to obtain a high aspect ratio, with concentric multilayers as the zone-plate rings. We have recently explored a linear zone-plate concept, by first growing a depth-graded multilayer on a flat substrate and then sectioning the multilayer and assembling several sections to focus the x-rays. The structure of the multilayer is calculated according to the desired focus parameters with corresponding Fresnel phase conditions. We have grown a depth-graded WSi@sub 2@/Si multilayer on a Si substrate using dc magnetron sputtering to test the linear zone-plate idea. The multilayer has a total of 469 alternating layers with thickness gradually increasing from ~15 nm to ~60 nm. It has a total coating thickness of ~11.27 µm and took ~45 h to coat. The sample has been sectioned and polished and studied using a scanning electron microscope and synchrotron radiation x-rays. The challenges and solutions for the growth of this kind of depth-graded multilayer will be discussed. @FootnoteText@ @footnote *@ This work is supported by the U. S. Department of Energy, under Contract No. W-31-109-ENG-38.

10:00am **SE-MoM6 Early Stages of Oxidation at 800°C for CrAlON Superlattice Coatings used to Improve Oxidation Resistance of Steel Plates for Applications as SOFC Interconnects@footnote *@***, **R.J. Smith**, A. Kayani, C.V. Ramana, P.E. Gannon, M.C. Deibert,* Montana State University-Bozeman*; V.I. Gorokhovsky,* Arcomac Surface Engineering, LLC*; V. Shutthanandan, D. Gelles,* Pacific Northwest National Laboratory

The requirements of low cost and high-temperature corrosion resistance for bipolar interconnect plates in solid oxide fuel cell stacks has directed attention to the use of metal plates with oxidation resistant coatings. We have investigated the performance of steel plates with superlattice coatings consisting of CrAlON (oxynitrides). The coatings were deposited using large area filtered arc deposition technology@footnote 1@, with various O/N pressure ratios, and subsequently annealed in air for up to 25 hours at 800°C. The composition, structure and morphology of the coated plates were characterized using RBS, nuclear reaction analysis, XPS and AFM techniques. Area specific resistance was measured as a function of time and temperature. By altering the architecture and composition of the coatings, the rate of oxidation was reduced by more than an order of magnitude relative to the uncoated steel plates. @FootnoteText@

@footnote 1@Vladimir I. Gorokhovsky, Rabi Bhattacharya and Deepak G. Bhat, Surface and Coating Technology, 140 (2) 2001, pp. 82-92.@footnote *@Work supported by DOI and DOE subcontract from PNNL, number 3917(413060-A). Work at PNNL (EMSL) supported through OBER (DOE) .

10:20am **SE-MoM7 Oxide Nanolaminate Coatings for Protection Against Perforated Pitting Corrosion in Stainless Steel***, **W.F. Gaertner**, C.R. Aita,* University of Wisconsin-Milwaukee

Perforated pitting corrosion is disastrous in stainless steel (SS) medical implants where even a low released cation concentration causes rejection by the surrounding tissue. Protection by oxide nanolaminates on 316L SS in saline is reported here. The behavior of constituent oxide single-layer films is also reported. We previously found [1] that a tetragonal ZrO@sub 2@/A1@sub 2@O@sub 3@ smart nanolaminate protects a rough 316L SS substrate (15 µm finish) against pitting. We constructed a model for corrosion prevention after a pit has initiated. This model involves mesoscopic film fracture accompanied by passivation of the underlying exposed SS. Here, we apply this model to (a) films on highly polished (1 micron finish) substrates where adhesion can be a problem, and (b) to a TiO@sub 2@/A1@sub 2@O@sub 3@ nanolaminate (which is not a smart coating) on both rough and substrates. 200 to 250 nm thick films were grown at room temperature by sequential sputtering of metal targets in Ar with 20% O@sub 2@ rf discharge. Cyclic polarization was used to determine the corrosion current, i@sub o@, as a function of applied potential after a steady state open circuit potential (OCP) was established. Samples were examined by scanning electron microscopy and energy dispersive spectroscopy. The results show that: (1) Corrosion current in all samples was low, on the order of 1 to 100 nA/cm@super 2@. (2) Single layer ZrO@sub 2@ and TiO@sub 2@ films did not protect against perforated pitting in polarized samples of either surface finish. (3) Single layer A1@sub 2@O@sub 3@ did prevent pitting but catastrophically failed after a single polarization cycle.(4) Nanolaminates protected by the synergic effect of a tough (ZrO@sub 2@, TiO@sub 2@) nanolayer combined with a brittle (A1@sub 2@O@sub 3@) became important in 316L SS with a rough finish. @FootnoteText@ NSF-CMS Grant No. 9988892 is acknowledged. [1]W.F.Gaertner,et al.,JVST A 22, 272 (2004).

10:40am **SE-MoM8 Environmentally Friendly Plasma Electrolytic Processes for Corrosion and Wear Protection of Lightweight Metals***, **A.L. Yerokhin**,* Sheffield University, UK, U.K.*; A. Matthews,* Sheffield University, UK **INVITED**

The paper discusses both fundamentals and applied aspects of novel Plasma Electrolytic Oxidation (PEO) processes which can be successfully used for wear and corrosion protection of Al, Ti and Mg alloys. Being a high-voltage electrochemical oxidation process, PEO is featured by a plasma discharge that occurs at the metal/electrolyte interface in the form of discrete short-lived microdischarges moving across the metal surface. This alters the kinetics of the main electrode processes, i.e. anodic oxidation and dissolution, complementing them with high rate gas evolution triggered by plasma enhanced thermochemical reactions at the metal surface. As a result, surface layers with composition and structure substantially different to those of conventional anodic oxide films can be formed in environmentally friendly diluted alkaline solutions. Electrolyte species tend to be more strongly incorporated into the surface layer, forming mixed oxide compounds. Rapid local heating and quenching of the surface during the microdischarge events promotes formation of high temperature oxide phases with fused-like structure, controllable porosity and a graded coating/substrate interface. Oxide ceramic surface layers produced by PEO as well as composite coatings based on these layers are proven to possess excellent tribological and anti-corrosion properties, which show promise for a number of industrial applications.

11:20am **SE-MoM10 Evaluation of Plasma Polymer Coatings in Corrosion Protection of Aluminum Alloys***, **Q.S. Yu**,* University of Missouri-Columbia, US*; Y.F. Chan, H.K. Yasuda,* University of Missouri-Columbia

As a pretreatment method, chromate conversion coatings are being widely used for corrosion protection of aircraft aluminum alloys. Pretreatment by chromate conversion layer is used to ensure good paint adhesion and provide corrosion inhibition. Due to the hazardous and toxic effects of chromates to environment and human heath, however, pressure from EPA has promoted research efforts focusing on the replacement of chromate conversion coatings with more environmentally friend systems. One promising alternative method is the use of plasma polymer coatings as pretreatment for metallic materials. Plasma polymerization process is a dry and â?ogreenâ?⍰ process which can produce high quality and chemically inert coatings with strong adherence to various substrates including metallic materials. Our recent studies have demonstrated that interface engineered plasma coating systems provide excellent corrosion protection of various aircraft Al alloys. In this study, the roles of plasma polymer coatings in interface engineering and fabrication of environmentally benign coating systems are further investigated. Electrochemical measurements including potentiodynamic polarization and electrochemical impedance spectroscopy are employed to characterize the corrosion resistance and interface properties of plasma coated Al alloys. The results obtained through this study will be presented and discussed.

11:40am **SE-MoM11 Nano-coatings for Complex Uneven Surfaces Cellular Foams & Nano-fibers of Carbon***, S.M. Mukhopadhyay, **R.V. Pulikollu**, P.P. Joshi,* Wright State University

The concept of surface coatings to enhance or prevent bonding with a second phase is not new, but when the surface in question has complex shape, and the coating needs to be effective at the nanometer scale, new challenges emerge. In this presentation, effectiveness of plasma-assisted nano-coatings (4-5nm thick) on two carbon structures will be presented. These are: (i) microcellular foam that has about 80% porosity and the surface consists of open, interconnected cell walls, and (ii) vapor-grown fibers having diameter of about 200nm. Both these structures are useful as reinforcing materials for composites. Coatings for enhancement surface wettability are obtained in microwave plasma using siloxanes. This treatment forms a strongly bound SiO2-type layer on the surface and causes noticeable enhancement of polar fluid infiltration in these materials. This results in micro-structural differences and enhancement of mechanical properties of composites formed. A different type of coating, that makes the surface inert by attaching CF2 groups on it, is effective in making these surfaces moisture-repellent. This coating appears to influence composite behavior in different ways. Additional aspects of these coatings, specific to different applications, such as bonding with metals and polymers, and possibility of creating multi-layer and multi-functional nano-coatings will be discussed.

Surface Science
Room 210B - Session SS1-MoM
Electronic Structure and Excitations

Moderator: P.S. Weiss, The Pennsylvania State University

8:20am **SS1-MoM1 Electronic Stablization of Nanophase Separation Along Si Atomic Chains***, **J.L. McChesney**[1],* University of Wisconsin*; J.N. Crain,* NIST*; V. Perez-Dieste, F. Zheng,* University of Wisconsin*; M.C. Gallagher,* Lakehead University, Canada*; F.J. Himpsel,* University of Wisconsin

One-dimensional surface structures have received a great deal of interest both for probing the fundamental physics phenomena of low-dimensions and for applications in nano-electronics. The Si(111)5x2-Au surface exhibits one-dimensional tracks with extra Si atoms on top, which have been used to demonstrate an atomic scale memory [1] and to probe the limits of storage density by studying the effects of inter-atomic coupling [2]. Atomic-interactions play a vital role in the determination of the electronic structure and vice versa. In an effort to elucidate this connection we used angle-resolved photoemission spectroscopy to probe the relevant electronic states in the vicinity of the Fermi level EF [3]. They are located at the zone boundaries of a 5x4 unit cell which explains the 5x4 periodicity of the inter-atomic potential [2]. This corresponds to the preferred spacing of the Si adatoms while the optimum chain doping would correspond to a 5x8 arrangement of the Si adatoms [4]. We propose that the nanoscale phase separation of this surface [5] into semiconducting 5x4 and metallic 5x2 sections is a way to accommodate these conflicting requirements. 1. R. Bennnewitz et.al., Nanotech. 13, 499 (2002). 2. A. Kirakosian et.al., Phys. Rev. B. 67, 205412 (2003). 3. J. L. McChesney et.al., submitted to Phys. Rev. B. 4. S. C. Erwin, Phys. Rev. Lett. 91, 206101 (2003). 5. H. S. Yoon et.al., Phys. Rev. Lett 92,096801 (2004). @FootnoteText@ .

8:40am **SS1-MoM2 The Hammett Equation in Single Molecule Chemistry: Probing a Linear Free Energy Relationship One Molecule at a Time***, B.V. Rao, K.-Y. Kwon, A. Liu, **L. Bartels**,* University of California, Riverside

Selective addressal of specific chemical bonds inside a molecule is at the heart of modern chemistry. With the advent of low-temperature scanning tunneling microscopy (STM), specific bonds of individual molecules became accessible in a controlled manner. Here we present how this technique may be applied to the study of a fundamental pillar of physical organic

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

chemistry, the Hammett Equation, one molecule at a time. Thiophenol and its halo/alkyl-substituted derivates adsorb on Cu(111) at 15K in a horizontal fashion leaving the thiol (-SH) group intact. Excitation by electrons of several hundred meV energy from an STM tip can induce selective dissociation of the SH-bond. This process is confirmed by STM-based vibrational spectroscopy of the S-H stretch mode. We measured the rate of electron-stimulated hydrogen abstraction for p-Fluoro-, p-Chloro-, p-Bromo-, p- Methyl-, m-Fluoro-, and m-Chloro-Thiophenol as well as for the unsubstituted species. The observed dehydrogenation rates follow the @sigma@-values of the Hammett equation, which were derived by pKs measurements on solutions of substituted benzoic acids 70 years ago. The positive @rho@ value of our measurements of 1.4 corresponds qualitatively to the solution phase value for thiophenols suggesting that a negatively-charged transition state is at the core of the STM-based hydrogen abstraction mechanism.

9:00am **SS1-MoM3 Benzene on Au{111} at 4 K: Observation of Molecular Cascades and Substrate-Mediated Interactions***, **P. Han**[1], E.C.H. Sykes, B.A. Mantooth, Z.J. Donhauser, P.S. Weiss,* The Pennsylvania State University

The role of the surface electronic structure was previously shown to have important implications on the long-range intermolecular interactions, molecular alignment and dynamics through substrate-mediated interactions (SMI) [1]. To date, attempts at quantifying SMI using scanning tunneling microscopy (STM) involve statistical measurements of STM images of static systems [2]. Here we present the study of benzene monolayer growth on a Au{111} surface using low temperature STM at 4 K. In this study, the tip-induced motion in the benzene overlayer was observed with 600 time-lapse STM images and it allowed us to statistically quantify the forces involved in SMI from a kinetic stand point. These estimates helped us explain the kinetics of the benzene motion, as well as the thermodynamics that determine the packing structure over the various regions of the reconstructed Au{111} surface. We also report the observation of tip-induced molecular cascade motion, and demonstrate that this observed motion is concerted in nature, not a result of individual random movements [3]. @FootnoteText@ [1] E. C. H. Sykes, P. Han, S. A. Kandel, K. F. Kelly, G. S. McCarty, and P. S. Weiss, Accounts Chem. Res. 36 (12), 945 (2003). [2] J. Repp, F. Moresco, G. Meyer, K. H. Rieder, P. Hyldgaard, and M. Persson, Phys. Rev. Lett. 85 (14), 2981 (2000); N. Knorr, H. Brune, M. Epple, A. Hirstein, M. A. Schneider, and K. Kern, Phys. Rev. B 65 (11) (2002). [3] P. Han, B. A. Mantooth, E. C. H. Sykes, Z. J. Donhauser, and P. S. Weiss, Accepted for publication by J. Am. Chem. Soc; E. C. H. Sykes, B. A. Mantooth, P. Han, Z. J. Donhauser, and P. S. Weiss, in preparation for J. Am. Chem. Soc.

9:20am **SS1-MoM4 Listening to Atom Dynamics During Atomic Manipulation***, **J.A. Stroscio**, R.J. Celotta,* National Institute of Standards and Technology

The physics of atomic manipulation with the scanning tunneling microscope (STM) involves many processes that depend on the tip-adatom interaction. We discuss our work on using atom manipulation imaging and the noise characteristics of the tunneling current as probes of the physics of the atomic manipulation process. By scanning a single Co atom across a Cu(111) surface, along the same path we would use to image the Cu surface, we can obtain a highly detailed image, showing three distinctly different atom binding sites. If the Co atom is positioned over an hcp site, dynamic behavior is observed both in the STM image and the tunneling current. The site dependent noise in the tunneling current is in the audio range and can be heard as the atom is dragged over the surface. We show that this dynamic behavior corresponds to state fluctuations of the Co atom; the Co hops between the hcp site and adjacent fcc sites. This occurs by the creation of an ideal, tunable, multi-well potential by the tip-adatom interaction. An ideal double-well potential can be created by positioning the Co atom slightly off the hcp site. Two-state transfer rates between the hcp and fcc sites are obtained by measuring the distribution of residence times in each state. The transfer rates show two distinct regimes. A transfer rate independent of tunneling current, voltage and temperature that is ascribed to quantum tunneling between the two wells, followed by a transfer rate with a strong power law dependence on current or voltage, indicative of vibrational heating. The role of these effects in atomic manipulation applications will be discussed.

9:40am **SS1-MoM5 Electronic Structure and Excitations at the Atomic Scale***, **W. Ho**,* University of California, Irvine **INVITED**

This talk will highlight the use of scanning tunneling microscopes (STM) to measure the electronic structure and elementary excitations at solid surfaces. The unique capabilities of the STM enable these measurements to be carried out with atomic resolution on single atoms, molecules, and nanostructures on solid surfaces. Electronic, vibrational, vibronic, plasmonic, and magnetic excitations will be discussed. These results provide a fundamental understanding of nanoscale properties and phenomena.

10:20am **SS1-MoM7 Quantum Well States in Thin Films of Pb on Si(111)***, **J.H. Dil**, J.W. Kim,* Fritz-Haber-Institute der MPG, Germany*; A. Mans, A.R.H.F. Ettema,* Delft University of Technology, The Netherlands*; K. Horn,* Fritz-Haber-Institute der MPG, Germany

The Pb/Si(111) system shows a rich variety of interesting physical properties and phenomena, such as the magic height of islands, vertical Friedel oscillations @footnote 1@, a competition between classical and quantum mechanical effects in the shape relaxation @footnote 2@, anomalous optical absorption @footnote 3@ and an anomalous behaviour in the Hall effect as a function of thickness. Hence it is important to study the electronic structure of thin Pb films on Si(111) with a view to understanding the origin of these phenomena. Photoemission experiments carried out at the synchrotron radiation facilities of MAX-lab in Lund (Sweden) and BESSY in Berlin, from a large range of film thicknesses prepared under different conditions exhibit clear signatures of 2 D quantum well states. Their energy dispersion with parallel electron momentum show an anomalously large in-plane effective mass of the 2D quantum well state bands, with the highest effective masses for states near the Fermi level. This contrasts with effective masses of the bulk bands from which these states are derived, and with similar data from the Pb/Cu(111) system @footnote 4@; also, band structure calculations for bulk and thin film slabs predict bands with predominantly free electron character. Our analysis suggests that this phenomenon may be due to a strong electron correlation effect in the 2D bands of the Pb quantum well states. @FootnoteText@ @footnote 1@ W.B. Jian, W.B. Su, C.S. Chang, T.T.Tsong, Phys.Rev.Lett.90, 6603 (2003). @footnote 2@ H. Okamoto, D. Chen, T. Yamada , Physical Review Letters 89, 6101 (2002). @footnote 3@ M. Jalochowski et al., Physical Review B 66, 205417 (2002). @footnote 4@ J.H. Dil, J.W. Kim, S. Gokhale, M. Tallarida, K. Horn, PRB, in press.

10:40am **SS1-MoM8 Newns-Anderson Model for Chemicurrents***, **S. Holloway**,* University of Liverpool, UK*; D. Bird, M. Mizielinski,* University of Bath, UK*; M. Persson,* Chalmers University of Technology, Sweden

The excitation of electron-hole pairs when a reactive species adsorbs on a surface should invariably be expected but it has proved difficult to quantify the strength of the process. We have performed first principles calculations for the interaction of a hydrogen atom with a Cu surface to investigate the chemicurrent induced. This calculation involves calculating the electronic response to the adsorbate motion and then using a forced oscillator description for the energy dissipation. Results will be presented for hydrogen and deuterium and comparison made with recent experiments. The numerical results are consistent with values derived from experiment for the H-Cu system. Application of the standard spin-polarised DFT approach results in a phase transition that occurs as the resonance intercepts the Fermi level. This, in turn, gives rise to an infinitely strong dissipative force above the metal which results in unphysical dynamics even before the atom encounters the adsorption well. The origin of the problem has been traced back to the nearly adiabatic assumption that is made in the standard application of time dependent DFT to electronic friction. In this present work, we deploy the Newns-Anderson description and show that this rather unexpected behaviour can be quite straightforwardly understood. Furthermore, we present for the first time, results for the chemicurrent using a new theoretical approach based on the time-dependent Newns-Anderson model.

11:00am **SS1-MoM9 Direct Observation of Electron Emission from a Metal Surface Due to Scattering of Vibrationally Excited Molecules***, **J.D. White**, J. Chen, D. Matsiev,* University of California, Santa Barbara*; D.J. Auerbach,* Hitachi Global Storage Technologies*; A.M. Wodtke,* University of California, Santa Barbara

We report the observation of electron emission from low work function metal surfaces due to the scattering of highly vibrationally excited nitric oxide (NO) molecules. Using Stimulated Emission Pumping (SEP) and Franck Condon Pumping (FCP), we prepare NO in vibrational states ranging from v=1 to v=18. SEP allows us to control explicitly the final vibrational state

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

(from v=4 to v=18) while FCP allows us to prepare a range of states (dependent on the Franck Condon Factors) from v=0 to v=5 in the Electronic Ground State. These molecules are then scattered off of a low work function surface (~1.3 - 1.6 eV), in our case submonolayer cesium on gold, and the emitted electrons are detected with a Multi Channel Plate assembly. Our experiments indicate that the observed particles are indeed electrons which are promptly emitted after collision of the vibrationally excited NO with the surface. Vibrational energy dependence experiments suggest a threshold for emission at roughly the work function of the surface. The maximum efficiency we have measured is approximately 0.02 electrons per molecule. Possible mechanisms for vibrationally induced electron emission are discussed. Our results are very important in determining the limitations of using the Born Oppenheimer Approximation (BOA) to model highly excited gas-surface reaction dynamics. The transition state for molecular dissociation very likely involves molecules stretched to large bond distances, which can be approximated by highly vibrationally excited molecules. Experiments along this vein will help to determine how accurate it is to use the BOA for modeling these systems.

11:20am **SS1-MoM10 Co-Adsorption of Polar Molecules with SF@sub6@ on Ru(0001): Effect on Adsorption Geometry, Ion Yields and Electron-Mediated Chemistry***, **D.O. Kusmierek**, N.S. Faradzhev, T.E. Madey,* Rutgers, the State University of New Jersey

SF@sub6@ is widely used as an electron scavenger for high voltage applications, and is a potent greenhouse gas; the electron-induced reactivity of gaseous and condensed SF@sub6@ is an environmentally important issue. The present work focuses on the effect of polar co-adsorbates H@sub2@O and NH@sub3@ on (1) adsorption geometry of SF@sub6@ on Ru(0001) at 25K, (2) formation and desorption probabilities of ions (F@super+@, F@super-@,) generated by electron stimulated desorption (ESD) of SF@sub6@, passing through condensed overlayers, and (3) chemical reactions activated by low-energy electrons. Electron stimulated desorption ion angular distribution (ESDIAD) and temperature programmed desorption (TPD) reveal predominantly molecular adsorption of SF@sub6@ on Ru(0001) via three F atoms, with the other three pointing away from the surface. Deposition of a polar molecule overlayer leads to changes in both intensities and trajectories of desorbing F@super+@ and F@super-@ ions. Low-energy electron-irradiation of SF@sub6@ films causes a step-wise decomposition of the molecules, and new chemical species are detected for electron-irradiated SF@sub6@ adsorbed on water (ice) surface. Analysis of the angular distributions of F@super+@ and F@super-@ as a function of temperature, co-adsorbate coverage and electron irradiation, in conjunction with TPD data, give insight into the structure of the molecular film, the ESD mechanisms, the ion/molecule scattering processes and the radiation chemistry observed here.

11:40am **SS1-MoM11 Spin-Resolved Plasmon Dispersion of Gd(0001)***, **H.-K. Jeong**, D.S. Wisbey, P.A. Dowben,* University of Nebraska-Lincoln

The spin-resolved plasmon dispersion, Ep(k//), of Gd(0001) on Mo(112) was investigated using spin-polarized electron energy loss spectroscopy. In spin polarized electron spectroscopy, the spin majority band structure of Gd(0001) exhibits different electron-phonon coupling than spin minority. There is some modest indirect evidence from the effective higher Debye temperature [1] derived from the spin minority bands than from the majority bands, but the compelling evidence arises from the spin dependence plasmon structure. Spin-polarized plasmon dispersion was observed. In addition to the spin-resolved plasmon dispersion, Ep(k//), we will show plasmon energies are dependent on primary energies and temperature. [1] Hae-Kyung Jeong, R. Skomski, C. Waldfried, Takashi Komesu, P. A. Dowben, E. Vescovo, "The Effective Spin Dependent Debye Temperature of Gd(0001)", accepted Physics Letters A (2004).

Surface Science
Room 210C - Session SS2-MoM

Functionalization of Semiconductor Surfaces

Moderator: J.N. Russell, Jr., Naval Research Laboratory

8:20am **SS2-MoM1 Atomic-level Control of Chemical Properties of Si(100) with Dopant Impurities***, Y. Wang, **G.S. Hwang**,* The University of Texas at Austin

Atomic-level manipulation of surface chemical properties becomes necessary for the fabrication of ever smaller semiconductor devices and a wide range of future molecular devices. The electronic structure of semiconductor surfaces can be modified by surface reconstruction, defects, impurities, and adsorbates. This will in turn alter physical and chemical processes occurring on the surfaces. One could envisage atomistic control of surface reactivity by incorporating dopant impurities into the surface or subsurface. A detailed understanding of the role of dopants as possible reaction promoters or inhibitors will contribute greatly to finding a new and reliable way to construct desired organic function assembly on semiconductors for various chemical, biological, and electronic applications. Using density functional theory calculations, we have looked at the modification of Si(001) surface properties by incorporating Boron and Phosphorous atoms into the surface and subsurface layer. We have found that surface (or subsurface) dopants bring about a significant change in surface chemical properties by altering surface polarization. As a result, chemical reactions on a dopant-modified surface show a distinctively different feature from on the clean surface. In this talk, we will present i) the effect of subsurface Boron on the surface reactivity of Si(001) based on water and ammonia adsorption and ii) auto-catalyzed molecular nanostructure formation of styrene on Si(001) using Phosphorous as initiator and terminator.

8:40am **SS2-MoM2 Chemistry on Surfaces of Thin Films and at Thin Film/Silicon Buried Interface: Vinyltrimethylsilane and (hfac)Cu(VTMS) on Si(100)-2x1 and on TiCN/Si(100)***, **A.V. Teplyakov**, L. Pirolli,* University of Delaware

Surface chemistry of vinyltrimethylsilane (VTMS) and (hfac)Cu(VTMS) on Si(100)-2x1 surface covered with several nm thick TiCN films formed from tetrakis-(dimethylamino)-titanium has been investigated using multiple internal reflection Fourier-transform infrared spectroscopy (MIR-FTIR), Auger electron spectroscopy (AES) and thermal desorption mass spectrometry. The structure of the films has been analyzed using time-of-flight secondary ion mass spectrometry and atomic force microscopy. This unique combination of surface analytical techniques allows one to follow chemical and physical changes at the surface of the system, within the thin film, and at the thin film/silicon interface. VTMS was found to adsorb molecularly both on Si(100)-2x1 and on the surface of the TiCN thin film at cryogenic temperatures (100 K), while it exhibits chemisorption if dosed at room temperature. Multiple reactions involving VTMS on both surfaces occur upon thermal annealing: molecular desorption around 400 K, formation and desorption of propylene by 500 K, decomposition leading to the release of silicon-containing products around 800 K. On a clean Si(100)-2x1, surface decomposition leading to the production of silicon carbide and the release of hydrogen takes place at 800 K. This chemistry is markedly different from the previously reported behavior of VTMS on Si(111)-7x7 surface resulting in 100% conversion to silicon carbide. (hfac)Cu(VTMS) chemistry, in particular the role of the VTMS ligand and the decomposition products, has also been studied both on clean Si(100)-2x1 and on a TiCN film deposited on silicon. A comparison of these studies with previous aluminum precursor chemistry will be discussed.

9:00am **SS2-MoM3 Functionalization of Semiconductor Surfaces***, M.A. Filler, D.W. Porter,* Stanford University*; A. Kim,* KAIST, Korea*; J.A. Van Deventer, **S.F. Bent**,* Stanford University **INVITED**

The growing importance of organic materials in electronic and optical technologies motivates the development of new attachment chemistries for combining organic layers with semiconductor substrates. We have investigated methods of functionalizing semiconductor surfaces by chemically reacting organic molecules at silicon and germanium surfaces in vacuum. These surfaces present intriguing templates for chemical reactions because the nature of the (100)-2x1 reconstructed surface of silicon and germanium yields dimers that can mimic the reactivity of organic functional groups. This behavior allows for the use of a wide variety of reactions to attach organic groups to the semiconductor surface. Our studies have explored the reactivity of a range of functional groups, including alkenes and dienes, amines, alcohols, carbonyls, nitriles, and isocyanates. The results of experimental and theoretical studies of the adsorption chemistry will be described in the context of several key mechanistic themes, including electrophilic/nucleophilic chemistry and [4+2], [3+2], and [2+2] cycloaddition reactions. Approaches for using these reactions for molecular layer deposition will be introduced, and some of the challenges in organic functionalization, including formation of inter- and intradimer products as well as coverage-dependent effects, will be discussed.

9:40am **SS2-MoM5 Adsorption of Amines on Germanium and Silicon Surfaces***, P. Prayongpan, **C.M. Greenlief**,* University of Missouri-Columbia

The bonding and structure of organic molecules with semiconductor surfaces is important for a variety of potential applications. This work examines the interactions between small organic molecules; ethylamine and allylamine, with Si(100)-2x1 and Ge(100)-2x1 surfaces. Ab initio calculations are used to investigate the transition states and predicted adsorption products for the reactions between the organic molecules and a dimer cluster model of the semiconductor surfaces. The cluster models include Si@sub 9@H@sub 12@, Ge@sub 9@H@sub 12@, and a mixed cluster; Ge@sub 2@Si@sub 7@H@sub 12@. Ultraviolet and x-ray photoelectron spectroscopy are used to examine the chemical bonding of the adsorbed products. This work will examine the effect of electron donating organic molecules with semiconductor surfaces. The selectivity and reactivity of functional groups in the surfaces will be described. According to our recent experimental and theoretical studies, the adsorption products for the interaction between amine molecules with Si(100)-2x1 and Ge(100)-2x1 surfaces are temperature dependent. Low temperature adsorption favors dative bonding of the amine with either surface, whereas different adsorption geometries are observed for adsorption at higher surface temperatures.

10:00am **SS2-MoM6 Silicon Surface Chemistry of Substituted Triazines***,* ***S.M. Casey****, L.M. LeMond,* University of Nevada, Reno

Deposition of substituted triazines onto the Si(100) surface was examined in order to investigate the initial stages of an organic molecular beam epitaxial growth approach to carbon nitride film formation. These reactions were probed under ultrahigh vacuum conditions using thermal desorption spectroscopy, Auger electron spectroscopy, and low-energy electron diffraction. Experiments reveal that the reactions of species such as 2-amino-1,3,5-triazine are self-limiting with a saturation coverage of about one molecule per four silicon surface atoms. Computational modeling of available reaction pathways was also performed using ab initio and density functional theory approaches. The results from these computations using cluster models of the silicon surface are consistent with the results from the experimental studies, and point to stable reaction products where the incident substituted triazine molecule bridges between two adjacent (within the same dimer row) silicon surface dimers.

10:20am **SS2-MoM7 Carbonyl Chemistry at the (100)-2x1 Semiconductor Interface***,* ***M.A. Filler****, S.F. Bent,* Stanford University

Several recent studies of the covalent attachment of organic molecules at group-IV (100)-2x1 semiconductor interfaces reveal that even for simple compounds, complex bonding geometries that may involve multiple surface dimers are probable. In an attempt to gain further insight into the fundamental thermodynamics and kinetics of intra- and interdimer bonding pathways, we have studied the reactions of acetone and acetaldehyde on Si(100)-2x1 and Ge(100)-2x1 using a combination of infrared and X-ray photoelectron spectroscopy. For the Ge(100)-2x1 surface, infrared data of both acetone and acetaldehyde reveal a low coverage peak near 1510 cm@super -1@. Isotopically-labeled derivatives of these compounds provide evidence that this mode corresponds to an interdimer adsorption product where a carbonyl moiety donates charge to a neighboring dimer atom. Additional absorption peaks are observed near 1675 cm@super -1@ for moderate surface coverages and at 1600 cm@super -1@ near saturation, likely resulting from @nu@(C=O) and @nu@(C=C) stretching modes, respectively. These data suggest that, in addition to the previously reported ene product, carbonyl-containing compounds can react to form a C-H dissociation product where the carbonyl moiety remains intact. Results will be discussed within the context of classical organic chemistry, mainly keto-enol tautomerization, acidity, and hydrate formation.

10:40am **SS2-MoM8 Adsorption of Chiral Enantiomers of 2,3 butanediol on Si(100)***, J.W. Kim,* Fritz-Haber-Institute der MPG, Germany*; M. Carbone,* Universita Tor Vergata, Italy*; M. Tallarida, J.H. Dil,* ***K. Horn****,* Fritz-Haber-Institute der MPG, Germany*; M.P. Casaletto,* Instituto per lo Studio die Materiali Nanostrutturati ISMN, Italy*; R. Flammini,* Istituto de Metodologie Inorganiche e dei Plasmi CNR, Italy*; M.N. Piancastelli,* Universita Tor Vergata, Italy

The adsorption of the chiral L,L- and R,R as well as the achiral R,L enantiomer of 2,3-butanediol on a Si(1 0 0) surface has been investigated by photoelectron spectroscopy. The valence band spectra show features assigned to molecular orbitals of 2,3-butanediol by comparison with calculations, and the surface states of clean Si are removed. The Si 2p reveals core-level shifts with two new components at 0.24 and 0.97 eV from the bulk, which are assigned to Si-H and Si-O bonds, respectively. The C 1s core-level spectrum consists of two major peaks separated by 1.3 eV, which are attributed to carbon atoms in -CHOH and -CH3 groups, in the molecule respectively. From the analysis of the valence band, the Si 2p, C 1s, and O 1s core-level spectra, we conclude that the 2,3-butanediol molecule undergoes a cleavage of the O-H bonds, and is bonded to the surface by the oxygen atoms. The molecule shows no further fragmentation and probably forms a six-membered ring of the O-C-C-O segment with the Si dimer atoms. By using circularly polarized x-rays we were able to observe a sizeable circular dichroism in the C1s core level emission from the different enantiomers. We discuss this finding in its potential to identify the presence of chiral centers in adsorbed molecules.

11:00am **SS2-MoM9 Self Assembly on Si(114)-(2x1): Molecular Attachment Via Alkene Functional Groups***,* ***D.E. Barlow****, A.R. Laracuente, L.A. Baker, L.J. Whitman, J.N. Russell, Jr.,* Naval Research Laboratory

Si(114)-(2x1) is a stable high-index surface oriented 19.5@degree@ between (001) and (111). Because the equilibrium surface reconstruction consists of a single domain of oriented, periodic rows of dimers, rebonded (001) steps, and non-rebonded steps, it is an ideal substrate for examining whether structure-specific reactivity can be used to create organic 1-D nanostructures on Si. We used STM and FTIR spectroscopy to study ethylene and cyclopentene chemisorption on Si(114)-(2x1) in ultra-high vacuum and to characterize the resulting degree of order at the organic-Si interface. Specifically, we examined the orientation, structure, and bonding arrangements of the adsorbates at the various sites on the Si(114) surface. STM and LEED show that well-ordered monolayers can be formed even on this heterogeneous surface. STM images show that the initial adsorption occurs preferentially along a single structural row, rather than by random occupation of multiple binding sites. Polarized transmission FTIR results are consistent with chemisorption of both ethylene and cyclopentene on Si(114)-(2x1) via [2+2] cycloaddition with preferential adsorbate orientation along the rows on the surface. The results clearly demonstrate that Si(114)-(2x1) is a suitable high index surface for organic self assembly using alkene cycloaddition chemistry.

11:20am **SS2-MoM10 Adsorption of Cata-condensed Aromatic Compounds on Si(100)***, K. Okamura, Y. Hosoi, Y. Kimura, H. Ishii,* ***M. Niwano****,* Tohoku University, Japan

We have investigated the adsorption of cata-condensed aromatic compounds on a Si(100)-2x1 surface using infrared absorption spectroscopy (IRAS) in the multiple internal reflection geometry (MIR). Si samples (prisms) used for MIR-IRAS measurements were prepared from n-type Si wafers and pre-cleaned by the conventional RCA treatment. The 2x1 reconstructed surface was obtained by flashing the sample surface at about 1300 @super o@C following thermal annealing at 900 @super o@C in an UHV chamber. To dose the 2x1 surface with small aromatic compounds (benzene, naphthalene and anthracene), we introduced them into the chamber in gas phase, while larger aromatic compounds were adsorbed on the surface by vacuum evaporation. We have collected IRAS spectra of those aromatic compounds adsorbed on the 2x1 surface, and analyzed the spectra in the region of C-H stretching vibration modes. It is well known that carbon in the sp2 coordinate exhibits absorption peaks in the region of 3000-3100 cm@super -1@, and carbon in the sp3 coordinate shows peaks in the region of 2900-3000 cm@super -1@. All of the measured spectra exhibited C-H stretching vibration peaks at both regions, indicating that some of the carbon atoms of the molecule are transformed from the sp@super 2@ to sp@super 3@ coordinate to form Si-C bonds when the aromatic compounds adsorb on the surface. We observed that these aromatics adsorb on the surface in different manners depending on the surface coverage. Compared with cluster calculation based on the density functional theory method, we determined that small aromatic compounds adsorb in a relatively simple conformation at low coverage, while high-coverage produces some complicated adsorption configurations. Larger aromatic compounds exhibited two different kinds of peaks; one is due to the molecule adsorbed directly on the Si surface (chemisrption), and the other is due to that adsorbed on the monolayer-covered surface (physisorption).

11:40am **SS2-MoM11 Ideal Methyl Termination of the Si(111) Surface***,* ***T. Yamada****, M. Kawai,* RIKEN, Japan*; A. Wawro,* Polish Academy of Sciences, Poland*; S. Suto, A. Kasuya,* Tohoku University, Japan

Si(111) surface ideally terminated by methyl (CH@sub 3@-) groups with a (1x1) periodicity was realized by Grignard reaction of Cl:Si(111)-(1x1). STM discerned a well-ordered (1x1) adlattice covering the Si(111) monoatomic step/terrace features as well as 3-fold-symmetric internal structure of protrusions corresponding to the CH@sub 3@ adsorbates. Reservation of all CH@sub 3@ internal bonds and formation of C-Si bond were confirmed by HREELS.@footnote 1@ Scanning tunneling spectroscopy (STS) exhibited diode-like I-V characteristics involving a new surface-originated occupied density of state at -1.6 eV. This unique electronic structure seems to be reflected on the electrochemical behavior in aqueous solutions. Measurement of vibrational decay time by laser sum-frequency generation is now in process for the internal modes. This finding of (1x1) adstructure led us to consider about the conditions of 2-dimensional ordering of organic moieties. Due to the C-Si covalent bonding, the adsorbates can hardly be mobile and self-assembling by inter-adsorbate interaction cannot be expected. Ordering should basically be originated by one-by-one termination of surface Si, and the adspecies should be accommodated within a hexagonal (1x1) unit cell of Si(111).@footnote 2@ We plan to deposit small moieties, such as CH:::C-, N:::C- and CF@sub 3@- by novel organic reagents. We also critically consider about deposition of long-chain alkyl adsorbates usually studied for purposes of application. The anchoring part of a long alkyl moiety sticks out of the (111) unit cell, and some of the neighborhood Si atoms should be terminated by small adsorbates (such as H and fragmented hydrocarbons). We attempted to approach this problem by investigating the surfaces formed by Grignard reaction with linear-chain alkyl groups (C4 and less). @FootnoteText@ @footnote 1@ T. Yamada et al., J. Am. Chem. Soc. 125 (2003) 8039.@footnote 2@ P. Allongue et al., J. Electroanal. Chem. 550 (2003) 161.

Thin Films
Room 303C - Session TF-MoM
ALD and Applications

Moderator: S.M. George, University of Colorado

8:20am **TF-MoM1 Atomic Layer Deposited Barriers for Copper Interconnects***, **J. Schuhmacher**, A. Martin, D. Ernur, Zs. Tőkei, Y. Travaly, C. Bruynseraede, A. Satta, C.M. Whelan, D. Shamiryan, G. Beyer,* IMEC, Belgium*; T. Abell,* Intel affiliate at IMEC, Belgium*; V. Sutcliffe,* Texas Instruments affiliate at IMEC, Belgium*; M. Schaekers, K. Maex,* IMEC, Belgium **INVITED**

Development and properties of a WNC atomic layer deposited (ALD) barrier film in terms of requirements and performance for damascene BEOL process flows are discussed. Damascene type substrates comprise various surfaces. The interaction of a surface with the ALD precursors controls the growth of ALD films. The effects of the substrate are reflected by the characteristics of the transient, non-linear growth period. Examples show the importance of characterizing the nature of the substrate / ALD interaction. Surface preparation before or during the ALD process is a useful tool for improving ALD film quality. An example for the challenges set by the introduction of a new material in an existing process flow is given with the interaction of ALD WNC to the chemical mechanical planarization (CMP) process. Film reliability will be discussed on damascene test structures with ALD WNC in the range of 2 to 10 nm.

9:00am **TF-MoM3 Effects of Surface Chemistry on ALD Ta(N) Barrier Formation on Low k Dielectrics***, **J. Liu**, J. Bao,* University of Texas at Austin*; M. Scharnberg,* Technische Fakultat der Christian-Albrechts-Universitat, Germany*; P.S. Ho,* University of Texas at Austin

For atomic layer deposition (ALD) of ultra-thin Cu barrier layers, the initial chemisorption at the substrate surface is important in controlling the barrier uniformity and morphology. It is particularly important for organosilicate (OSG) low k dielectrics generally characterized by inactive surface bonds which have to be properly activated for sufficient ALD nucleation. In-situ x-ray photoelectron spectroscopy (XPS) was employed to study the effects of the surface chemistry on ALD Ta(N) barrier formation on two main types of low k surfaces, OSG and SiLK. The initial chemisorption was confirmed to be through formation of Ta-O bonding on OSG films and charge transfer complexes on the aromatic SiLK films. The evolution of the low k surface chemistry revealed an initial transient growth region controlled mainly by the substrate surface chemistry. Pre-treatment of the OSG low k surfaces with nitrogen and hydrogen radical beams, particularly with nitrogen radicals, was observed to enhance significantly the chemisorption of the TaCl@sub 5@ precursor on the OSG surfaces. The enhancement was attributed to the dissociation of the weakly bonded methyl groups from the low k surface followed by surface nitrogen enrichment. The improvement of the growth rate observed in this study illustrates the criticality of the surface coverage at saturation for a successful ALD process. In the subsequent linear growth region, atomic hydrogen species was able to reduce the chlorine content under appropriate temperature and with sufficient purge. The role of the atomic hydrogen in this process enhancement is discussed. In addition, precursor penetration was observed to be suppressed as a result of surface activation on the mesoporous OSG, suggesting a possible approach to pore sealing of porous OSG with halide ALD chemistry.

9:20am **TF-MoM4 Evaluation of Plasma Enhanced Atomic Layer Deposition TaN for Metal Gate Electrode Application***, **H. Kim**,* IBM Thomas J. Watson Research Center*; D.-G. Park, P. Ronsheim,* IBM Semiconductor Research and Development Center*; S.M. Rossnagel,* IBM Thomas J. Watson Research Center

TaN has been one of the most attractive materials as a diffusion barrier for Cu interconnect technology due to its good diffusion barrier properties, good adhesion to dielectrics, and high thermal stability. More recently, TaN has been considered as a strong candidate for a direct metal gate material due to its proper work function (~4.3eV) as n-type conductivity. As for the deposition technique of metal gate electrode, previous study on TiN metal gate demonstrated that atomic layer deposition (ALD) has benefits including negligible defect generation and improved device reliability compared to other deposition method. Previously, we have reported that PE-ALD from TaCl@sub 5@ and N@sub 2@/H@sub 2@ plasma produced low resistivity cubic TaN films with various N/Ta ratios with excellent barrier properties for Cu metallization. In this study, PE-ALD TaN was evaluated as a gate electrode for metal-oxide-semiconductor (MOS) capacitors composed of TaN/SiO@sub 2@/p-Si with nanoscale thick (1.8-5.5 nm) SiO@sub 2@ dielectric. For as-patterned MOS structure, the leakage current characteristics were strong functions of N/Ta ratio and plasma power. A dramatic decrease of leakage current with two orders of magnitude was observed with decrease of the plasma power from 500W to 200W. For PE-ALD TaN electrode with stoichiometric N/Ta ratio, we observed a severe damage at SiO@sub 2@/Si interface as observed by a distorted capacitance-voltage (C-V) curve shape near the valence band edge of Si band gap. While the interface damages were partially disappeared after forming gas anneal, the gate leakage current level was remained high. However, the reduction of leakage current was more prominent for TaN@sub x@ films deposited with N@sub 2@ only plasma at both high and low plasma power condition with improved C-V characteristics. Additionally, a comparative study with PVD TaN electrode will be presented focusing on the impurity effect of TaN metal gate.

9:40am **TF-MoM5 Nucleation and Electrical Characterization of Ruthenium formed by Selective Area Atomic Layer Deposition***, **K.J. Park**, J.M. Doub, G.N. Parsons,* North Carolina State University

Ruthenium is a promising candidate for advanced metal gate electrodes in complementary metal-oxide-semiconductor (CMOS) transistors because of its thermal stability and low resistivity. Ru metal films were deposited by Atomic Layer Deposition (ALD) in a flow tube reactor system using Ruthenocene with oxygen as a reducing reactant on hydrogen terminated silicon, silicon oxide, HfO@sub 2@, as well as patterned organic monolayer surfaces at temperatures ranging from 300 to 375°C. Films were characterized by Auger electron spectroscopy, atomic force microscopy, and capacitance voltage analysis. Self limiting ALD behavior with ~1Å/deposition cycle was observed between ~315 and 350°C at 1.2 Torr operating pressure. At higher temperatures, growth rate per cycle increased indicating the onset of CVD growth conditions. No growth was observed at 300°C on any surface indicating no precursor adsorption, consistent with previous studies of the ruthenocene/oxygen ALD process. The incubation time for deposition was strongly dependent on the substrate. Growth initiated quickly on chemical oxide whereas >100 cycles were required for growth on Si-H surfaces and methyl terminated organic monolayers. The difference in nucleation allowed for selective area deposition of Ru on micron-scale pre-patterned surfaces, where >300Å of growth proceeded on oxide, with no visible deposition on the organic monolayer. Capacitor structures were formed by selective Ru deposition and characterized electrically using various thicknesses of dielectric films. Fitting the flatband voltage vs thickness results in an effective workfunction of 4.8eV on SiO@sub 2@, indicating that selective area deposition may be useful for integration of multiple metals into dual-metal gate CMOS structures. Possible mechanisms associated with nucleation and substrate dependence will be discussed.

10:00am **TF-MoM6 Atomic Layer Deposition for Metal Gate and Capacitor Electrodes***, **D.-G. Park**,* IBM Microelectronics **INVITED**

An employment of atomic layer deposition (ALD) method into the semiconductor devices is becoming pivotal because of the excellent attributes offered by ALD process such as good coverage and low impurity level. The ALD technique provides thin film depositions of nanoscale high-permittivity (k) gate dielectrics, metal electrodes, deep metal contact fill, and liners and/or barrier layers of Cu. This paper will review and discuss about the properties of thin ALD films for direct metal gate and capacitor electrodes. As a direct metal gate electrode application, various ALD metal electrodes such as TiN, TaN, and WN films were evaluated on thin SiO2 and high-k gate dielectric films for metal-oxide-semiconductor (MOS) capacitors and transistors. The effects of impurities and process conditions on the MOS devices will be discussed. MOS devices gated with ALD thin films demonstrated much lower defect densities than those with sputtered films by means of lower interface trap density and orders of magnitude lower leakage current. This is most likely a result of the relatively damage-free ALD deposition process. Equivalent oxide thickness of sub-nanometer (< 1nm) was attained with ALD-metal/high-k stack against the thermal budget of complementary MOS device fabrication. Additionally, an application of ALD-TiN film into a capacitor electrode for extremely high aspect ratio (~ 70:1) trench capacitors for sub-100nm trench DRAM devices will be presented. It is necessary to keep focusing on the development of various ALD materials systems to meet device requirements such as relevant work function and stability across the required thermal cycle.

10:40am **TF-MoM8 Infrared Analysis of HfO@sub2@ ALD from Hafnium Diethyl-Amide on SiO@sub2@ and Si-H surfaces***, **M.J. Kelly**, G.N. Parsons,* North Carolina State University*; J.G. Han, C.B. Musgrave,* Stanford University

An important advantage of atomic layer deposition is the potential to control bond structure at the initial growth interface. Deposition of high dielectric constant metal oxides on silicon typically leads to substrate oxidation and uncontrolled interface structure. To explore mechanisms in interface layer growth, we have used attenuated total internal reflection infrared spectroscopy to study of HfO@sub2@ formation on Si-OH and Si-H terminated surfaces from a tetrakis (diethylamido)hafnium metal organic precursor. Precursor exposure at 200°C on the Si-OH surface results show self-limiting chemisorption consistent with formation of Hf-O-Si bonds with substantial Hf-ethylamine ligands remaining. Exposing the surface to H@sub2@O results in removal of C-H modes, consistent with surface oxidation and formation of Hf-OH surface units. Precursor chemisorption is also observed on the Si-H starting surface, likely due to reaction with some surface OH. Distinct changes in the surface Si-H stretching modes are observed upon precursor adsorption, possibly due to interactions between the amine ligands and the surface hydrogen. Exposing this surface to H@sub2@O does not completely oxidize the surface products, consistent with alternate stable surface bonding configurations, likely involving formation of Si-C or Si-N bonds. Ab-initio results describing potential mechanisms of precursor dissociation and Si-H/ligand interactions will be discussed.

11:00am **TF-MoM9 Area-selective Atomic Layer Deposition for high-@kappa@ Dielectric Materials***, **R. Chen**, D.W. Porter, S.F. Bent, H.S. Kim, R. Sreenivasan, P.C. McIntyre, H. Jagannathan, Y. Nishi,* Stanford University

Atomic layer deposition (ALD) is a technique that can be used to deposit a variety of materials. While ALD inherently provides nano-scale control of materials in the vertical direction, we are investigating an area-selective ALD technique that enables micro- and nano-scale definition of the lateral structure. Our research emphasizes controlling the substrate surface chemistry in order to impart spatial selectivity to ALD. Using a variety of analytical techniques, we show that functionalizing the surface with self-assembled monolayers (SAMs) can block the ALD chemistry in the growth of HfO@sub 2@ and ZrO@sub 2@, which are both high-@kappa@ materials for potential gate dielectrics. Specifically, we have investigated the surface chemistry needed to block ALD under the more extreme conditions used to deposit these metal oxide dielectrics from metal chloride and water precursors at temperature as high as 300 °C. The efficiency of blocking depends strongly on the quality of the SAMs and the chain length of the attached layer. The potential of the area-selective process for defining lateral structure has been examined using different patterning methods, including selective functionalization of patterned SiO@sub 2@/Si and soft lithography. Using a combination of image analysis by SEM and elemental analysis by scanning Auger microscopy, we demonstrate that the HfO@sub 2@ can be deposited with spatial selectivity. Other types of SAMs have also been investigated as monolayer resists against the HfO@sub 2@ ALD process on Si and Ge substrates. These monolayer films also exhibit good deactivation and selectivity.

11:20am **TF-MoM10 SiO@sub 2@ Atomic Layer Deposition Using HSi[N(CH@sub 3@)@sub 2@]@sub 3@ and H@sub 2@O@sub 2@***, **B.B. Burton**,* University of Colorado*; S.W. Kang,* Pohang University of Science and Technology, Korea*; S.M. George,* University of Colorado

The atomic layer deposition (ALD) of SiO@sub 2@ has proven to be challenging. SiO@sub 2@ ALD can be accomplished using SiCl@sub 4@ and H@sub 2@O reactants at 600-800 K with large exposures of ~10@super 9@ L. Catalytic SiO@sub 2@ ALD is also achieved at room temperature with the same reactants but requires the presence of a Lewis base catalyst. Recently, we have observed efficient SiO@sub 2@ ALD with HSi[N(CH@sub 3@)@sub 2@]@sub 3@ and H@sub 2@O@sub 2@ reactant exposures. HSi[N(CH@sub 3@)@sub 2@]@sub 3@ is tris-dimethylaminosilane (Tris-DMAS). SiO@sub 2@ ALD was monitored on high surface area ZrO@sub 2@ particles that allowed the use of Fourier transform infrared (FTIR) spectroscopy to monitor the surface chemistry. Following the H@sub 2@O@sub 2@ exposures, the surface displayed vibrational modes consistent with SiOH* species. Tris-DMAS exposure at 825 K converted these species to Si-N(CH@sub 3@)@sub 2@* species and SiH* species. The subsequent H@sub 2@O@sub 2@ exposure converted these species back to SiOH* species. The exposures required for Tris-DMAS and H@sub 2@O@sub 2@ were ~10@super 6@L and ~10@super 7@L, respectively. These exposures are much more favorable than the ~10@super 9@ L exposures required to grow SiO@sub 2@ ALD films with SiCl@sub 4@ and H@sub 2@O at 600-800 K. Other advantages of using Tris-DMAS are the avoidance of HCl as a byproduct and the elimination of possible chlorine contamination in the SiO@sub 2@ film. The SiO@sub 2@ thin films were deposited at temperatures ranging from 525-825 K. The maximum growth rate of 1.9 Å/cycle at 825 K was determined by measuring the SiO@sub 2@ film thickness on ZrO@sub 2@ particles by transmission electron microscopy (TEM). When the temperature was decreased below 825 K, residual SiH* species were observed in the film and led to a decrease in the SiO@sub 2@ ALD growth rate. SiO@sub 2@ growth was also confirmed by the increase in absorbance from the Si-O-Si asymmetric stretch measured by FTIR spectroscopy.

11:40am **TF-MoM11 Radical-Enhanced Atomic Layer Deposition of Pure and Erbium-Doped Y@sub 2@O@sub 3@ Thin Films***, T.T. Van, **J.P. Chang**,* University of California, Los Angeles

The deposition of pure and Er-doped yttrium oxide thin films, using radical-enhanced ALD (RE-ALD), was investigated in this work. Yttrium oxide can be used as a high dielectric constant material, or as a waveguide material due to its high refractive index and compatibility with high concentration doping of optically active Er@super 3+@ ions. The Y@sub 2@O@sub 3@ films were deposited on Si using alternating pulses of Tris(2,2,6,6-tetramethyl-3,5-heptanedionato)yttrium(III) precursor, or Y(TMHD)@sub 3@, and O radicals. Erbium dopants were incorporated by introducing Er(TMHD)@sub 3@ after every ten ALD cycles of Y@sub 2@O@sub 3@. To assess the feasibility of RE-ALD, X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), atomic force microscopy (AFM), and scanning electron microscopy (SEM) were used to determine the chemical composition and distribution, crystallinity, surface morphology, and step coverage of the deposited films. Well-controlled RE-ALD of pure Y@sub 2@O@sub 3@ and Er@sub 2@O@sub 3@ were achieved with both precursors and O radicals. With reactant pulse time ratio of 1:1, stoichiometric films were deposited with minimal carbon incorporation. The ALD window for both materials ranged from 200 to 300°C. Above 300°C, the precursors decomposed, causing significant carbon incorporation into the films. AFM analysis yields a root mean square roughness of less than 5Å for films below 110Å. Conformal deposition of Y@sub 2@O@sub 3@ was achieved over 0.5-µm features with an aspect ratio of 4, determined by cross-sectional SEM. The Er@super 3+@ doping concentration was effectively controlled by varying the ratio of Y@sub 2@O@sub 3@:Er@sub 2@O@sub 3@ cycles. For example, up to 8 at.% of Er@super 3+@ concentration was achieved at 300°C with alternating 10 cycles of Y@sub 2@O@sub 3@ and 5 cycles of Er@sub 2@O@sub 3@. These results indicate that RE-ALD is a viable technique for doping and depositing metal oxide thin films.

Applied Surface Science
Room 210A - Session AS-MoA

SIMS II - Biological and Organic

Moderator: G. Gillen, National Institute of Standards and Technology

2:00pm **AS-MoA1 Single Photon Ionization of a Derivatized Peptide Covalently Bound to a Surface***, P.D. Edirisinghe, S.S. Lateef, C.A. Crot,* ***L. Hanley****,* University of Illinois at Chicago*; J.F. Moore, W.F. Calaway, M.J. Pellin,* Argonne National Laboratory

Covalently bound peptides, proteins, and other biomolecules are widely used for microarrays, microfluidic channels, cell growth surfaces, and biosensors. Detection of these surface bound species by matrix assisted laser desorption ionization or secondary ion mass spectrometry (SIMS) is often complicated by low ionization yields and/or high fragmentation. Single photon ionization is one method that shows great promise for enhancing ionization yields with a minimum of fragmentation. The fluorine excimer laser is an intense laboratory source of vacuum ultraviolet radiation, but the 7.87 eV photons it generates are lower in energy than the ionization potential of many target species. A method is described here whereby derivatization of peptides with the Fmoc group allows efficient fluorine laser single photon ionization of the entire labeled peptide. Various Fmoc labeled peptides are covalently bound to oxidized Si(100) wafers via maleimide coupling to surface bound aminopropyltriethoxysilane. Physisorbed films of Fmoc labeled peptides, unlabelled peptides, and various amino acids are prepared by drying a solution thereof onto the silicon wafer. Both covalently bound and physisorbed peptides are analyzed by laser desorption photoionization (LDPI) mass spectrometry. Only the Fmoc labelled peptides form large ions identified as common peptide fragments bound to either Fmoc or the surface linker. Unlabelled peptides and amino acids do not form large representative ions. Electronic structure calculations performed with Gaussian 98 indicate the Fmoc label is behaving as an ionization tag for the entire peptide, lowering the ionization potential of the complex below the 7.87 eV photon energy. This method should allow detection of many molecular species covalently or electrostatically bound to surfaces.

2:20pm **AS-MoA2 ToF-SIMS Applications in the Analysis of DNA Microarrays***,* ***K.K. Soni****,* Corning Incorporated

DNA arrays are typically prepared by microcontact printing of DNA on a glass surface that has been modified by an aminosilane. The DNA immobilization on the modified glass surface relies on direct contact between DNA and amine groups supplied by the silane layer. The presence of surfactants such as Triton even at trace level can completely inhibit attachment of DNA. Given the tendency of this molecule to segregate at interfaces, its detection by surface sensitive techniques such as ToF-SIMS is facilitated; in other words, the sample preparation method and ToF-SIMS analysis constitute a very sensitive analytical procedure to detect trace levels of surfactant molecules in DNA preparations. To further corroborate the impact of surfactants, pure DNA solutions were intentionally contaminated with Triton X-100 in varying concentrations. The resulting mixtures were used for printing on modified glass slides. It was demonstrated that the presence of Triton reduces the amount of immobilized DNA and above a certain concentration (10-100 ppm by volume) can completely inhibit DNA printing. In another application of ToF-SIMS, we demonstrate the ability to study fluid flow and evaporation dynamics in a drying droplet in microarrays. Evaporation behavior of the drop strongly influences the solute transport and hence the uniformity of the dot. We have utilized ToF-SIMS analysis of printed DNA dots to determined the final distribution of the solute by mapping the sodium concentration in the drop. Three different kinds of effects were observed: the first kind having higher concentration of solute on the outer edge of the drop (rim effect); the second kind having higher concentration at the center of the drop (pinprick) and the third having uniform distribution.

2:40pm **AS-MoA3 Cell Imaging, DNA Diagnostics, Protein Analysis: Mass Spectrometric Characterization of Biological Surfaces***,* ***H.F. Arlinghaus****,* Physikalisches Institut der Universität Münster, Germany **INVITED**

We have used time-of-flight secondary ion mass spectrometry (TOF-SIMS) and laser postionization secondary neutral mass spectrometry (Laser-SNMS) to analyze various biological surfaces. Both techniques use a focused energetic primary ion beam for bombarding a solid sample, and a mass spectrometer for analysis. But unlike SIMS, which analyzes only the sputtered secondary ions, Laser-SNMS uses laser beams to either resonantly or non-resonantly ionize the majority of sputtered neutral particles. In our presentation, we will compare and discuss the salient characteristics of the TOF-SIMS and Laser-SNMS techniques and will show applications in the following fields: (a) imaging and quantifying target-specific drug delivery systems as well as intrinsic elements and molecules in single cells with subcellular resolution in vitro, i.e. in cell cultures, and in vivo, i.e. in tissues, (b) investigation of the immobilization process of PNA and the influence of length and type of spacer molecules on the efficiency of hybridizing DNA to PNA biosensor chips and investigation of its use for DNA diagnostics with unlabeled DNA, (c) detection of proteins in cells, and (d) investigation of yield behavior and fragmentation patterns using different primary ions (Ar@super +@, Xe@super +@, SF@sub 5@@super +@, Au@super +@, Au@sub n@@super +@) for increasing efficiency and sensitivity in cell and DNA diagnostics. Furthermore, we will discuss current instrumental developments, particularly in regard to 3D molecular imaging with nanometer-scale resolution. We will show that TOF-SIMS and Laser-SNMS are well suited for imaging and quantifying trace element and molecule concentrations in biological materials with very high efficiency and nanometer-scale resolution. In particular, TOF-SIMS has the potential for providing a new method for rapid unlabeled DNA diagnostics, and its high detection efficiency makes this technique especially useful for directly analyzing genomic DNA.

3:20pm **AS-MoA5 Molecular Depth Profiling of Polymer Multilayers using a Polyatomic Primary Ion Beam***,* ***M.S. Wagner****,* National Institute of Standards and Technology

Obtaining characteristic molecular information during the secondary ion mass spectrometry (SIMS) depth profiling of polymers has been severely limited due to primary ion-induced sample damage when using monatomic primary ions. Polyatomic primary ions have shown promise for the molecular depth profiling of thin (< 250 nm) polymer films due to their low penetration depth and high sputter rates. In this study, dual-beam time-of-flight SIMS (sputter ion = 5 keV SF@sub 5@@super +@, analysis ion = 10 keV Ar@super +@) was used to depth profile spin-cast multilayers of poly(methyl methacrylate), PMMA, poly(hydroxyethyl methacrylate), PHEMA, and trifluoroacetic anhydride-derivatized PHEMA, TFAA-PHEMA, on silicon substrates. Despite extended SF@sub 5@@super +@ bombardment (> 5 x 10@super 14@ ions/cm@super 2@), characteristic pendant-group-related positive and negative secondary ions of the different polymer layers were observed as a function of depth during the depth profiles. The sputter rates of the polymers in the multilayers typically were lower than corresponding single layer films, with the ion-induced damage accumulation rate of the outermost polymer layer affecting the sputter rate of the underlying layers. Due to its higher ion-induced damage accumulation rate, PHEMA lowered the sputter rates for underlying PMMA or TFAA-PHEMA layers. Similarly, PMMA reduced the sputter rate for underlying TFAA-PHEMA layers. Typical interface widths between adjacent polymer layers were 10-15 nm for the bilayer polymer films; however, the layer order significantly impacted the interface widths for trilayer films. The interface widths in the trilayer films increased with depth to ~ 35 nm, showing the formation of sputter-induced surface roughness during depth profiling of these films. This study demonstrates the utility of polyatomic primary ions for molecular depth profiling and presents new opportunities for the characterization of thin polymer films.

3:40pm **AS-MoA6 Applications of Cluster SIMS for Molecular Depth Profiling in Biomaterial Systems***,* ***C.M. Mahoney****,* National Institute of Standards and Technology*; J.-X. Yu, J.A. Gardella, Jr.,* State University of New York at Buffalo*; A.M. Johnson, R. Langer,* Massachusetts Institute of Technology

Polymeric biomaterials have numerous clinical applications including as surgical implants, absorbable sutures, tissue engineering scaffolds and drug delivery devices. Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS) has proven to be particularly useful in the surface analysis of these polymeric biomaterials@super 1@. However, much of this work has been done with monoatomic primary ion beams, which have a large amount of beam-induced damage associated with them. This precludes the ability to obtain in-depth information from organic samples. Compared to monoatomic ion bombardment, cluster primary ion beams, such as SF@sub 5@@super +@ have resulted in decreased subsurface damage and increased sputter rates in some cases, allowing the ability to depth profile in organic and polymeric materials for the first time@super 2-3@. This talk will briefly describe the ongoing research efforts at NIST to further develop cluster SIMS as a tool for biomaterials characterization. We have already shown the ability to depth profile in model polylactic acid (PLA) based drug delivery systems using cluster SIMS@super 3@. More recently, we have been able to successfully measure the extent of preferential segregation in polylactic acid / polyethylene glycol (PLA/PEG) blends as well as determine the in-depth distribution of acetamidophenol doped PLA films as a function of increasing degradation time. We have also successfully obtained information as a function of depth in a novel drug delivery microchip. This work further demonstrates the increasing utility of cluster SIMS for biomaterials applications. @FootnoteText@ @footnote 1@ Lee, J.-W.; Gardella, J.A. Jr. Analytical Chemistry 75 (2003) 2950-2958.@footnote 2@ Gillen, G.; Roberson, S.; Rapid Commun. Mass Spectrom. 12 (1998) 1303.@footnote 3@ Mahoney, C.M.; Roberson, S.V.; Gillen, J.G. in "Depth Profiling of 4-Acetamidophenol Doped Poly(lactic Acid) Films Using Cluster SIMS"; Analytical Chemistry, Accepted March 2004.

4:00pm **AS-MoA7 Improved ToF-SIMS Ion Yields and Cationization of Water-Soluble Analytes by Polyelectrolyte Multilayers***, **Y.-Y. Lua**, C.A. Pew,* Brigham Young University*; A. Schnieders,* ION-TOF USA, Inc.*; P.B. Savage, R.C. Davis, M.R. Linford,* Brigham Young University

Arguably one of the most important issues that has faced time-of-flight secondary ion mass spectrometry (ToF-SIMS) since its inception more than 30 years ago is the need for improved ion yields from analytes. Here we describe an entirely new method for improving ion yields and cationizing analytes that is particularly effective for charged, water-soluble species. This approach takes advantage of the highly charged, ionic nature of polyelectrolytes and the ease with which they can be deposited onto surfaces by the well known layer-by-layer method. In particular, we show that after an ultrathin film (ca. 0.5 nm) of a polycation (polydiallyldimethylammonium chloride, PDADMAC) spontaneously adsorbs onto a silicon (oxide) surface, a mixture of a polyanion (poly(sodium 4-styrenesulfonate)) and a water-soluble analyte, which contains one or more basic nitrogen atoms, will adsorb to form a second layer (ca. 1.5 nm thick). ToF-SIMS of this bilayer shows a significant enhancement in quasi-molecular analyte ion yield (roughly a ten-fold increase in signal), compared to that of the pure compound, or the compound dissolved in dilute HCl and dried on a surface. This phenomenon is demonstrated for two large organic macrocycles (m/z 672 and 745), and a smaller aromatic compound (acridine, m/z 179). Similarly, a significant enhancement in the ion yield of the quasi-molecular ion of 9-anthracenecarboxylic acid (m/z 222) is observed when it spontaneously deposits with PDADMAC to form a ca. 0.5 nm film on silicon.

4:20pm **AS-MoA8 Three-Dimensional Reconstruction of Elemental Distributions from TOF-SIMS Image Depth Profiles***, **S.R. Bryan**, D.G. Watson,* Physical Electronics USA

Time-of-flight Secondary Ion Mass Spectrometery (TOF-SIMS) is a powerful techique for image the distribution of elements and organic molecules on surfaces with with spatial resolution down to 100 nm. When combined with sputter depth profiling, TOF-SIMS can characterize the 3-dimensional distribution of all elements in the near surface region of materials. Due to the parallel detection nature of the TOF-SIMS technique, the full 3-dimentional data can be acquired for all elements in a reasonable amount of time. The challenge is to effectively display the tremendous amount of information generated in an image depth profile. The use of one or two cross-section images does not adequetly display the 3-dimensional distributions. In this work, we have applied methods developed in the medical field for CT and MRI imaging to TOF-SIMS data. Through the use of isosurface reconstruction and translucent display, the full 3-dimensional distribution of multiple elements can be viewed simultaneously.

Biomaterial Interfaces
Room 210D - Session BI-MoA
Protein-Surface Interactions

Moderator: P. Cremer, Texas A&M University

2:00pm **BI-MoA1 Thermodynamic and Kinetic Control of Protein Adsorption on Surfaces with Grafted Polymers***, **I. Szleifer**,* Purdue University **INVITED**

Grafted polymer layers modify the effective interactions between proteins and surfaces resulting in a change of the ability of the proteins to adsorb on the surface. Grafted polymers have a strong effect on both the equilibrium amount of proteins` adsorbed as well as in the kinetics of adsorption. In this talk we will review some of our understanding of the molecular parameters that determine the ability of polymer layers to reduce protein adsorption. We will present a theoretical approach that enables the study of both the kinetics and thermodynamics of adsorption. The predictions of the theory are in excellent quantitative agreement with experimental observations for the adsorption of proteins on surfaces with grafted (short and long) polyethylene oxide. We will show the role of polymer chain length and surface coverage on both the equilibrium adsorption isotherms and the kinetics of protein adsorption. For example, we find that for fixed polymer surface coverage there is a polymer molecular weight above which the equilibrium adsorption becomes independent of polymer chain length. However, the kinetics of protein adsorption depends very strongly on polymer molecular weight under all conditions. The time dependent adsorption is a very complex process due to the changes in the effective surface-protein interactions as the adsorption process progresses. Namely, the changes in the structure of the polymer layer as the proteins adsorb result in large changes in the kinetic process. We will show under what conditions the predicted equilibrium amount of protein adsorbed is finite, however, the time scale for adsorption is so slow that the layer completely prevents protein adsorption for practical purposes. Finally, we will show how chemical modifications of the polymer layer can be used to manipulate the amount, structure and time scale for adsorption and desorption of the proteins from the modified surface.

2:40pm **BI-MoA3 Approach Towards Protein Adsorption, Desorption and Exchange***, **M. Halter**,* ETH Zurich, Switzerland*; G. Szöllösi, I. Derényi,* Eötvös University, Hungary*; J. Vörös,* ETH Zurich, Switzerland

When an artificial object is introduced into a biological environment, its surface is covered almost instantly with a protein layer. Being such a crucial issue for any biological application, the processes involved in protein adsorption, desorption and exchange are still not fully understood. Many controversial theories about the reversibility or irreversibility of protein adsorption, whether an adsorbed layer is static or forming a dynamic equilibrium and other puzzles and paradoxes exist. We present a realistic model for protein adsorption that can adequately describe the observed experimental data, such as irreversibility, history dependence, or the Vroman effect. A novel instrument, the Single Channel Grating Coupler, was used to provide new insight into protein behavior at interfaces. It is a planar waveguide technique that uses the evanescent field generated by an incoupled laser beam. Fluorescently labeled proteins within this field are excited and emit a fluorescent signal. The major advantages of this instrument are its high sensitivity (lower detection limit < 10 fmol/cm@super 2@) and the possibility to measure protein exchange by varying the labeled to unlabeled protein ratio in a solution. In situ measurements of interfacial exchange reactions provide sufficient data to develop a sophisticated protein adsorption model. It assumes that each protein molecule has several different conformations in the adsorbed state with different footprint sizes and binding energies, separated by energy barriers. Numerical simulations of large numbers of proteins - supplemented by analytical calculations - allow us to reproduce the experimental data and identify the conformations of proteins. Such a model will hopefully lead to a better understanding of protein behavior at interfaces. Beyond this, knowledge of the processes involved will help to tune the important parameters to build up and control adsorbed protein layers as desired for specific applications.

3:00pm **BI-MoA4 Mixology of Protein Solutions and the Vroman Effect***, **A. Krishnan**, C.A. Siedlecki, E.A. Vogler,* Pennsylvania State University

Mixing rules stipulating both concentration and distribution of proteins adsorbed to the liquid-vapor(LV) interphase from multi-component aqueous solutions are derived from a relatively straightforward protein-adsorption model. Accordingly, proteins compete for space within an interphase separating bulk-vapor and bulk-solution phases on a weight, not molar, concentration basis. This results in an equilibrium weight-fraction distribution within the interphase that is identical to bulk solution. However, the absolute interphase concentration of any particular protein adsorbing from an m-component solution is 1/mth that adsorbed from a pure, single-component solution of that protein.Applied to adsorption from complex biological fluids such as blood plasma and serum, mixing rules suggest that there is no energetic reason to expect selective adsorption of any particular protein from the mixture. Thus, dilute members of the plasma proteome are overwhelmed at the hydrophobic LV surface by the thirty classical plasma proteins occupying the first-five decades of physiological concentration. Mixing rules rationalize the experimental observations that(i)concentration-dependent liquid-vapor interfacial tension of blood plasma and serum cannot be confidently resolved,even though serum is substantially depleted of coagulable proteins(e.g. fibrinogen) and(ii) of plasma is startlingly similar to that of purified protein constituents. Adsorption-kinetics studies of human albumin (66.3 kDa) and IgM (1000 kDa) binary mixtures revealed that relatively sluggish IgM molecules displace faster-moving albumin molecules adsorbing to the LV surface. This Vroman-effect-like process leads to an equilibrium reflecting the linear combination of w/v concentrations at the surface predicted by theory. Thus, the Vroman effect is interpreted as a natural outcome of protein reorganization to achieve an equilibrium interphase composition dictated by a firm set of mixing rules.

3:20pm **BI-MoA5 Molecular Dynamics Simulation of the @gamma@ Chain Fragment of Fibrinogen on Functionalized SAM Surfaces***, M. Agashe, S.J. Stuart,* ***R.A. Latour,*** Clemson University

Protein adsorption to biomaterials surfaces is a primary governing factor of biocompatibility. While much has been learned, the molecular mechanisms involved in adsorption behavior are not understood. Empirical force field based molecular simulation methods provide an excellent approach to theoretically investigate the molecular behavior of proteins as they adsorb to surfaces. In this research, molecular dynamics simulations were conducted to investigate the adsorption behavior of a 30kDa C-terminus fragment of the @gamma@ chain of fibrinogen (Fg) as a function of surface chemistry. Simulations were conducted using the GROMACS program and force field. The surfaces were modeled to represent Au-alkanethiol self-assembled monolayers (SAMs) with 5 surface functionalities: CH3, OH, NH2, COOH, and PEG. The model system consisted of Fg in saline (explicit water with Na+ and Cl- ions) positioned over a SAM surface. Systems were contained within a 105Å x 107Å base x 80Å high simulation cell with periodic boundary conditions. 5ns simulations were performed and the effects of adsorption on Fg were analyzed. The results predict that only minor changes in Fg conformation occur during this time frame, however, Fg was observed to undergo large surface-dependent rotational and translational motions, suggesting faster kinetics for reorientation than unfolding. Although contingent on the accuracy of the GROMACS force field, which has not yet been validated for this application, these results have profound implications for surface design because they suggest that surface chemistry should be an effective means to control the orientation of adsorbed proteins.

3:40pm **BI-MoA6 The Effects of Adsorbed Proteins on the Performance of Biomedical and Biotechnological Devices***,* ***T.A. Horbett,*** University of Washington **INVITED**

Proteins are abundant in biological fluids, readily adsorb to most devices that contact such fluids, and often adversely affect the performance of the device. For example, adsorbed proteins are believed to lower the biocompatibility of implants in the body, non-specific adsorption of antibodies interferes in many solid phase immunoassays, and protein adsorption to the walls of microfluidic devices can cause analyte loss and/or reductions in separation efficiency. In this presentation, I will first give a series of examples illustrating the role of adsorbed proteins in device related problems. A brief review of the major mechanisms of protein adsorption affecting device performance will be given, namely variations in affinity of proteins for surfaces and differences in the ability of adsorbed cell adhesion proteins to support cell adhesion ("molecular potency"). Alterations in molecular potency have often been ascribed to denaturation of adsorbed proteins. However, studies from Norde's lab have shown that adsorbed proteins that exhibit no thermal unfolding enthalpy, and thus appear to be completely denatured, actually retain considerable structure, so these important findings will be presented. In many situations, reducing cell adhesion to a surface is desirable, but ways to accomplish this are not always clear. Towards that end, studies in my lab of platelet and monocyte adhesion to adsorbed fibrinogen have suggested biomaterial design criteria to reduce cell adhesion that are based on the concepts of reducing molecular potency or affinity. Adsorbed proteins sometimes have low molecular potency, but the properties of the surface which cause it are unclear, so it is currently difficult to apply this criteria in designing new surfaces. In contrast, the other design criteria, a need for ultralow fibrinogen affinity surfaces, has been used to make better surfaces, as will be illustrated with glow discharge deposited tetraglyme, and with polyurethanes with added PEO.

4:20pm **BI-MoA8 The Surface Analysis and Quantification of the Electro-sprayed Fibronectin on Biocompatible Materials***,* ***M.J. Wang,*** Queen Mary University of London, UK, United Kingdom*; D.A. Lee, M.D. Paine, D.L. Bader, J.P.W. Stark,* Queen Mary University of London, UK

Electrospray is employed as a novel technique to incorporate biomolecules on substrates because it provides the possibility of soft landing the biomolecules. The interactions between biomolecules and substrates are, first of all, examined by surface analysis techniques such as atomic force microscopy (AFM) and Fourier Transform Infrared (FTIR) to identify the efficiency of electrospray and examine the morphology of the biomolecules. Moreover, the immunofluorescent methods provide the possibilities of gaining both quantitative and qualitative information. Fibronectin (FN) was chosen as the target molecule to be sprayed due to its functionalities such as promoting proliferation, differentiation of cells, also to promote the cell-cell and cell-substratum adhesion. Silicon wafer and medical grade stainless steel are chosen as target substrates due to their surface energy and biocompatibility. Both FTIR and AFM analysis show the effective landing of fibronectin via electrospray. The landed fibronectin shows the characteristic peaks of amide I and amide II compositions of fibronectin. Moreover, the linear relationship for the concentration of fibronectin versus the intensity of characteristic peaks of fibronectin by FTIR indicates that FTIR could serve as a semi-quantitative technique for examining the fibronectin. On the other hand, the AFM can detect the existence of Fibronectin up to the single molecule scale. The image shows the double strains of FN which is similar as the morphology of FN found in reference (Ref). Moreover, by immunofluorescence analysis, the efficiency of using electrospray to deposit FN on the substrates can be identified. And a quantitative assessment of the biomolecules on the substrates can be provided. These results provide potential possibilities of patterning array and assemblies of tissue which could be applied in the drug discovery and biosensors fields.

4:40pm **BI-MoA9 The Effect of Surface Structure and Functionality on Conformation of Surface-Adsorbed Fibrinogen***,* ***C.L. Berrie****, J.E. Headrick, K.L. Marchin, S. Phung,* University of Kansas

The interactions of the plasma protein fibrinogen with surfaces have been studied using atomic force microscopy (AFM). Specifically, well-characterized model substrates have been used to investigate the effect of surface chemistry and structure on the adsorption of fibrinogen. Dramatic differences in the average size and shape of fibrinogen molecules adsorbed to hydrophobic and hydrophilic substrates have been observed. These changes can be readily seen in AFM images of individual molecules with sub-molecular resolution. The differences have been quantified and correlated with the surface chemistry. In addition, new methods for patterning nanostructured substrates for use in these experiments have been investigated as well as methods for chemically functionalizing AFM probe tips in order to obtain information beyond topography. Adsorption of fibrinogen on nanostructured thin films and the effects of ionic strength and pH of the solution will also be discussed.

Materials Solutions for Cooling Technology Topical Conference
Room 303B - Session CT-MoA

Material Solutions for Chip Cooling

Moderator: C.R.K. Marrian, IBM Almaden Research Center

2:00pm **CT-MoA1 Natural Power Scaling Trends in Microprocessors and Other Complex Logic***,* ***E.A. Burton,*** Intel Corporation **INVITED**

The last decade has seen a continual growth in the size and complexity of cooling solutions for mainstream personal computers. Natural CMOS scaling trends, and the competitive nature of the electronics industry, have been the twin drivers of this aggressive cooling technology trend. Every 18 months a new silicon processing node is developed, which doubles the number of transistors that can be packed into a given sized die. Although these new transistors are half the area of the ones they replace, they are faster and have a higher capacitance density. The end result is an exponential power scaling trend with a doubling of power every few years. This trend is clearly evident in Central Processing Units (CPUs), where the power has increased roughly 10x in a decade. The same exponential power-growth trend is also showing up in graphics processor chips (GPUs), where recent high-end products sport dual-slot cooling solutions with heatpipes, fans, and ducted airflow.@footnote 1@ Although at first glance the roughly 10x per decade power-scaling trend would seem to signal impending disaster, a reduction in the performance vs. time ramp can immediately stop the power ramp. Market forces will be the deciding factor in setting the future power vs. time ramp. Integrated circuit manufacturers will have to plan their future performance ramp carefully to ensure the ramp is economically sustainable. Since the future performance trend will be limited largely by the capability and affordability of the cooling technology, integrated circuit cooling has taken on a profoundly strategic importance. Since exponentially shrinking the flagship die-area is an obvious means of stopping the future power ramp, even a constant power vs. time is likely to present a serious cooling challenge. A fixed power limit combined with steadily shrinking die sizes results in steadily increasing power density. Such a trend presents an obvious materials challenge, or perhaps a strategic opportunity - depending on one's point of view. This paper explores the underlying silicon scaling trends driving the increasingly important field of integrated circuit cooling. Since increasingly difficult and costly cooling will change the underlying scaling trends, altered scaling scenarios are also studied. These altered scaling studies are not intended to be an exhaustive optimization, but rather to explore sensitivity or likely range of difficulty a materials scientist might expect to face in the future. It is hoped this will set the stage for following papers, which delve deeper into actual cooling materials science. @FootnoteText@@footnote 1@http://www6.tomshardware.com/graphic/20040414/geforce_6800-05.html

2:40pm **CT-MoA3 Challenges and Opportunities for Cooling Advanced Semiconductor Devices**, ***D. Seeger,*** IBM T.J. Watson Research Center **INVITED**

As CMOS technology continues to evolve, direct scaling has become increasingly difficult. As a result, the rules of scaling have been 'fudged' in order to stay on the historical Moore's law curve. In particular, power has not decreased at a rate consistent with Moore's Law though chip area has scaled. As a result, chip power densities are increasing rapidly. Chip power densities for CMOS technologies today rival that of bipolar devices of the last decade. At that time, the industry was focused on developing advanced chip cooling technologies to deal with the high powered bipolar devices of the time. However much lower power CMOS device technology came along to 'save the day' and allowed most of these advanced chip cooling technologies to be shelved. Today we face a similar situation for chip power densities. However there is no comparable low power technology on the horizon and as a result, the power density problem must be solved. In thinking about this problem from the chip to the package, the first surface the chip faces is typically a heat spreader made of copper or other high thermal conductivity material. In order to insure good thermal contact, a thermal interface material (TIM) is sandwiched between the chip and the heat spreader. These materials are two orders of magnitude better in thermal conductivity than air, hence the reason for their existence. However, they are typically two orders of magnitude LOWER in thermal conductivity than the other materials in the chip/package stack. Given that this is the most important interface in the stack, a lot of focus has been placed on improving the thermal conductivity of TIMs. Since the heat spreader has a significantly different thermal coefficient of expansion than the chip, compliant mechanical considerations are also important. Then, intimate thermal contact to an efficient heat sink must be accomplished. Once at the heat sink level, the heat must be expelled to the air and then carried out through the computer box, racks in the case of servers. Finally, this heat needs to be removed from the data center. All of the above components must be optimized as a system since any single point in the thermal path can choke off the flow of heat and dramatically decrease the efficiency of heat removal from the system. This talk will be an overview of these issues and the technologies being developed to overcome them

3:20pm **CT-MoA5 Overview of the Heat Removal by Thermo Integrated Circuits (HERETIC) Program at the Defense Advanced Research Projects Agency (DARPA)**, ***D.J. Radack,*** Defense Advanced Research Projects Agency (DARPA) **INVITED**

The objective of the HERETIC program is to develop solid-state and fluidic heat removal devices that are integrable with dense, high-performance electronics and photonics. These devices are envisioned to short-circuit the thermal resistance between heat sources and thermal sinks; they should also lead to a reduction in overall system volume and weight. It is expected that devices will be designed for high efficiency operation (in terms of work done to remove a unit of heat from a hot junction). Traditional thermal management in many electronic and optoelectronic systems is generally relegated to the end of the process sequence in the packaging of the systems. For non-critical applications, where the systems are used in relatively benign environments, this approach is cost-effective and has worked well. This ad hoc method of thermal management is inadequate and the need for new or novel approaches becomes clear for certain situations. These situations may be: where the system package must be small and compact; where the density of high-performance, high-power chips on a board is high; or where the environment is thermally harsh. In conventional thermal management, heat removal or cooling is typically addressed hierarchically. The first level of the hierarchy is at the system level, the second is at the board level, and the third is at the chip-package level. As a common example, consider the following case: at the system (box) level, global air circulation may be effected by a fan that blows over boards that comprise the system; at the board level, the chips may be mounted on a board that allows the circulation of a coolant through it; and, at the chip-package level, the package (containing a telecommunications laser chip or a special processor chip, for example) could be cooled directly by a thermoelectric cooler. The focus of this program is at chip and board levels.

4:00pm **CT-MoA7 Liquid Cooling Technologies for Microprocessors**, ***T.W. Kenny****, K.E. Goodson, J.S. Santiago,* Stanford University*; M. Munch, G. Upadhya, D. Werner, M. McMaster,* Cooligy, Inc. **INVITED**

Recent trends in processor power for the next generation devices point clearly to significant increase in processor heat dissipation over the coming years. In the desktop system design space, the tendency has been to minimize system enclosure size while maximizing performance, which in turn leads to high power densities in future generation systems. The current thermal solutions used today consist of advanced heat sink designs and heat pipe designs with forced air cooling to cool high power processors. However, these techniques are already reaching their limits to handle high heat flux, and there is a strong need for development of more efficient cooling systems which are scalable to handle the high heat flux generated by the future products. To this end, a new closed loop liquid cooling system has been developed to handle heat fluxes greater than 500 W/sq cm. The cooling system comprises a micro channel heat exchanger for high heat flux removal capability, an electro-kinetic pump for delivering fluid with required flow rate and pressure, coupled with a counterflow heat rejecter to dissipate heat to the ambient. This talk will describe the components of this technology and discuss the process taken to transition from DARPA-Funded academic research to venture-funded startup to successful company.

4:40pm **CT-MoA9 Microfluidic Technologies for Integrated Thermal Management**, ***A. Glezer,*** Georgia Institute of Technology **INVITED**

The development and demonstration of microfluidic-based, thermal management technologies for a diverse range of heat loads [O(10)-O(1000) W] are described. These technologies address both local and global stages of heat transport between integrated circuits and the environment into which the heat is ultimately rejected. The fluidic-based cooling approaches range from phase-change heat transport based on vibration-induced droplet atomization (VIDA) and vibration induced bubble ejection (VIBE), to controllable heat convection using micromachined synthetic air jet arrays. Examples of the implementations of these technologies include the integration of synthetic jet actuators with heat sink configurations to form an "active" heat sink, and with electronic substrates (e.g., printed wiring boards) to form an active cooling substrate (ACS), as well as the realization of compact, VIDA- and VIBE-based, phase-change heat transfer cells.

Electronic Materials and Processing
Room 304B - Session DI-MoA

High-k Dielectrics: Electronic Properties

Moderator: T. Klein, The University of Alabama

2:00pm **DI-MoA1 Metal Nitride Gate Electrode Effects on Dielectric Properties of HfO2 and Hf-doped TaOx High-k Gate Dielectrics**, ***Y. Kuo****, J.-Y. Tewg, J. Lu,* Texas A&M University*; P. Majhi, G. Bersuker,* Sematech

High-k gate dielectrics with appropriate gate electrodes are critical to future MOS device performance. Metal oxides, such as hafnium oxide and various doped tantalum oxides, are promising high-k materials. Since polysilicon has many practical limits for the high-k gate electrode application, e.g., undesired interface layer formation and dopant diffusion, other conductive materials are being actively sought for this purpose. Metal nitrides are possible candidates because they can be easily prepared by the sputtering method, are usually difficult to react with the adjacent oxide, and are good diffusion barriers. In this paper, authors investigated the influence of various types of metal nitride electrodes, i.e., molybdenum nitride MoN, tungsten nitride WN, and tantalum nitride TaN, on electrical characteristics of MOS capacitors composed of a high-k dielectric layer of hafnium oxide or Hf-doped tantalum oxide. Hafnium oxide was deposited by atomic layer deposition ALD and the doped tantalum oxide was deposited by reactive sputtering. Dielectric properties, such as EOT, leakage current, flatband voltage, metal work function, and interface state density, were studied. Process parameters, such as the annealing temperature and atmosphere were varied for their influence on the electrical properties. The interface and bulk film material properties were characterized with ESCA, XRD, and TEM. Dielectric properties were dramatically influenced by the nitride electrode and the process parameters. We are going to discuss the cause of the difference with respect to material and interface layer changes during the process.

2:20pm **DI-MoA2 d-states Coupling in Mixed High-k Oxides: Transition Metal Oxide Binary Alloys, and Transition Metal-rare Earth Complex Oxides***, **G. Lucovsky**, C.C. Fulton, Y. Zhang, J.L. Whitten, R.J. Nemanich, H. Ade,* NC State University*; D.G. Schlom,* Penn State University*; J.L. Freeouf,* Oregon Research Institute*; Y. Zou,* NC State University

The lowest conduction band anti-bonding d*-states in (HfO@sub 2@)@sub x@(TiO@sub 2@)@sub 1-x@ pesudo-binary alloys, and in TiO@sub 2@ and HfO@sub 2@ have been studied by soft x-ray absorption spectroscopy (XAS). These studies distinguish between intra-atomic transitions within the Ti- and Hf-atoms and inter-atomic transitions that involve mixing of the Ti and Hf d*- and s*-states with O 2p*-states. Comparisons between the energies of the lowest d*-states in the O K@sub 1@ spectra of TiO@sub 2@ and HfO@sub 2@ indicate that the energy difference between these features is essentially the same as the energy difference between d*-state features at the respective band edges. There are systematic changes in the d*-state features of the alloys that are consistent with the coupling of valence band d-states of Ti- and Hf-atoms through bonding a common O-atom. This mixing has confirmed through complementary changes in the valence band electronic structure as deduced from ultra-violet photoelectron spectroscopy (UPS). Ab initio quantum chemistry molecular orbital calculations indicate that d-state coupling is maximized when the respective d-states of the Ti- and Hf-atoms have the same symmetry, and the Ti-O-Hf bonding group is collinear. This results in two coupled modes. The O K@sub 1@ edge spectrum of a HfTiO@sub 4@ film (x = 0.5), crystallized by annealing at 800°C, shows three d*-features, indicating that the coupling of Hf 5d*- and Ti 3d*-states is not optimized. Non-optimized coupling of d*-states associated with a dynamic Jahn-Teller effect has also been found in the complex lanthanide rare earth/transition metal oxides, Gd(Dy)ScO@sub 3@. Non-optimized d-state coupling is also evident in band edge spectra. The relationships between d-state coupling and band gap engineering of high-k dielectrics will be discussed.

2:40pm **DI-MoA3 Theoretical Analysis of High-K Dielectric Interfaces with Silicon and Metals***, **A.A. Demkov**,* Motorola, Inc. **INVITED**

The scaling of the complimentary metal oxide semiconductor (CMOS) technology requires the replacement of silicon dioxide with a high dielectric constant (high-k) material as a gate dielectric. Having a high-k film in the gate stack results in a capacitance equivalent to a much thinner film of a dielectric with a lower dielectric constant. The benefits of a high-k material are thus twofold, a higher capacitance results in a higher saturation current and improves the performance, and the increased thickness cuts down the gate leakage current and improves the power consumption. Successful implementation of a high-k dielectric in CMOS depends upon our ability to control the interfacial properties. The chemistry at the Si/dielectric and dielectric/electrode interfaces is determined by atomic-scale interactions, which ultimately sum to yield the electrical properties such as the threshold voltage observed macroscopically. A rigorous attempt to predict and control the interface behavior, therefore, must be based on the atomic-scale characterization and first-principle calculations. In this talk I will review the recent theoretical work on the interfaces of high-k dielectrics with Si and metals, and in particular, the calculations of the band alignment at the interface. I will discuss relative advantages of amorphous vs crystalline oxides (including epitaxial oxides). A connection will be made to the device characteristics such as the threshold voltage by means of using the results of density functional calculations in TCAD simulations.

3:20pm **DI-MoA5 Nitrided Hafnium Silicates for Gate Dielectrics***, **C.-G. Wang**, H. Velasco, M. Verghese, E. Shero, G. Wilk,* ASM America Inc.*; J.W. Maes, O. Laitinen,* ASM International, Belgium*; W. Deweerd, A. Delabie,* IMEC, Belgium*; R.L. Opila, A. Mathew, K. Demirkan,* University of Delaware*; J. Morais, I.J.R. Baumvol,* Universidade Federal do Rio Grande do Sol, Brazil

Nitrided hafnium silicate (HfSiON) gate dielectric films deposited by atomic layer chemical vapor deposition (ALCVD@super TM@) show excellent capacitor and transistor characteristics with both poly-Si and metal gates, which are directly correlated with local physical and chemical properties. A wide range of compositions are demonstrated, with Si/(Hf+Si) percentages from 0 to 75% and uniformly distributed N levels up to 30 at. %. XPS is used to distinguish the local bonding arrangements of N to Hf, Si and O. The distribution and depth profile of these N bonds is directly attributable to the observed electrical and physical properties of these films as measured by TOF-SIMS, TEM, EELS, nuclear reaction analysis and angle-resolved XPS. Using poly-silicon gate electrodes with chemical or thermal oxide underlayers, EOT values down to 1.3 nm with substantial leakage reduction vs. SiO@sub 2@ have been achieved using stacks with ultrathin HfSiON. Hysteresis and midgap interface density (D@sub it@) are less than 10 mV and 5X10@super 10@ cm@super -2@eV@super -1@, respectively. Transistors (gate length of 110nm) with these ALD HfSiON films display excellent V@sub T@ stability and channel electron mobility > 90% of SiO@sub 2@ at high E@sub eff@. Detailed analysis on silicate compositions, the distribution of nitrogen in the interface layers, and corresponding impact on device performance will be presented.

3:40pm **DI-MoA6 Optical Properties of Prospective High-k Dielectric Films***, **E. Cicerrella**, J.L. Freeouf,* OGI School of Science & Engineering of OHSU*; L.F. Edge, D.G. Schlom,* The Pennsylvania State University*; T. Heeg, J. Schubert,* Inst. fur Schicht und Ionentech., Germany*; S.A. Chambers,* Pacific Northwest National Laboratory

The current gate dielectrics in silicon MOSFETs are unable to prevent excessive gate leakage as devices continue to shrink. The effort continues to establish appropriate materials to replace SiO2 to remove this problem. New processing issues arise as we deal with these new materials â?" especially as they are deposited on Si substrates. We have established that some rare earth perovskites have high dielectric constants. We believe that they will be thermodynamically stable with silicon and therefore are possible gate dielectrics. We discuss thin films of one candidate material, LaScO3, which were grown by molecular beam deposition on Si substrates and pulsed laser deposition on MgO substrates. Using spectroscopic ellipsometry in the Far UV (5 eV - 9 eV) and the UV/VIS (1.5 eV - 5 eV), as well as transmission studies between 1.5 eV and 6 eV, we have established that low temperature deposition leads to a reduced band gap and a lower density as compared with the bulk crystal. We seek to understand the impact of deposition technologies as well as other process steps, such as high temperature anneals. To this end we have had high temperature anneals performed on these films and then repeated these measurements and analysis. In this analysis we shall seek changes in density, band gap, refractive index, and interfacial layers between the substrate and the deposited film.

4:00pm **DI-MoA7 Spectroscopic Studies of Valence Band States in HfO2, TiO2, ZrO2 and HfTiO4 by Soft X-Ray and Vacuum Ultra-Violet Photoemission Spectroscopy***, **C.C. Fulton**, G. Lucovsky,* North Carolina State University

Valence bands of HfOsub@2@, TiO@sub 2@, ZrO@sub 2@ and HfTiO@sub 4@ films have been studied by soft x-ray photoemission spectroscopy (SXPS) at energies between 70 and 170 eV, and by He I and II ultra-violet photoemission spectroscopy (UPS) at energies of 21.2 and 40.8 eV. For HfO@sub 2@, SXPS studies reveal two valence bands as well as the Hf 4f doublet, whereas He I UPS studies have probed only the uppermost valence band. SXPS and UPS energies are referred to an extrapolated threshold energy at 8.1±0.2 below vacuum, or ~3 eV below the valence band edge of c-Si. The first SXPS valence band has features at 2.2±0.2 eV and 6.2±0.2 eV. The 4f doublet components are at 13.7±0.2 eV and 15.4±0.2 eV. The second valence band is centered at ~22 eV. The UPS valence band displays features at 1.5±0.2 eV and 5.2±0.2 eV. Energies of the symmetry determined valence band molecular orbitals have been obtained from ab intio calculations on relatively small clusters. The top of the valence band is assigned to O 2p @pi@ non-bonding states. With this as a reference, calculated MOs are: Hf 5d @pi@ + O 2p @pi@ at 0.5±0.2 eV and Hf 5d @sigma@ + O 2p @sigma@ at 5.4±0.2 eV, with an energy difference of 4.9±0.3 eV, and O 2s at 22.2±0.2 eV. Setting the valence band edge to the O 2p p non-bonding energy, and averaging SXPS and UPS spectra, the experimental MOs in the first valence band are at 1.8±0.2 eV for Hf 5d @pi@ + O 2p @pi@, and 5.7± eV for Hf 5d @sigma@ + O 2p @sigma@, with an energy difference of 3.9±0.3 eV. The O 2p @pi@ non-bonding and Hf 5d @pi@ + O 2p @pi@ bands overlap and contribute to a broad spectral feature, and this resulting agreement between theory and experiment is good. The average energy of the O 2s band is 22±0.3 eV, and is in excellent agreement with the calculated energy of 22.2 eV. The paper will also include SXPS and UPS valence band studies for TiO@sub 2@, ZrO@sub 2@ and HfTiO@sub 4@.

4:20pm **DI-MoA8 Electronic Properties and Band Alignments of Hf-based Gate Dielectrics on Silicon***, **R. Puthenkovilakam**, J.P. Chang,* University of California, Los Angeles

Ultra thin HfO@sub 2@ or HfO@sub x@N@sub y@ thin films are being considered for possibly replacing SiO@sub 2@ gate oxide in silicon based metal-oxide-semiconductor (MOS) transistors. In this work we investigated the electronic structure and band alignments at the HfO@sub 2@(or HfO@sub x@N@sub y@)/Si interfaces which dictate the device performance of transistors in the sub-90nm devices. We used tetragonal structure to model HfO@sub 2@ and nitrogen incorporation was achieved by replacing selective oxygen atoms with nitrogen. The electronic structure of HfO@sub 2@/Si interface showed dangling bond states at the interface due to the reduced coordination of Hf caused by the intrinsic bond constraints at the HfO@sub 2@/Si interface. However, our calculations indicate that these dangling bonds could be passivated by hydrogen or oxygen, which can appropriately change the coordination numbers at the interface, thereby removing the dangling bond states. We also considered the interface of HfSiO@sub 4@/Si and found that there are no dangling bond states at this particular interface, making HfSiO@sub 4@ a promising interfacial layer to improve the interface quality. Band offsets at the HfO@sub 2@/Si interfaces were theoretically calculated and showed that the conduction band offsets ranged from 1.5-1.9 eV depending upon the interface stoichiometry. Band offsets were experimentally determined by measuring the core level to valence band maximum binding energy differences using XPS and were in excellent agreement with the theoretical results. Incorporation of nitrogen into the HfO@sub 2@ network resulted in notable changes in the valence band structure of the material and the corresponding band alignments with silicon and is found to depend on the nitrogen concentration in the bulk of HfO@sub 2@ as well as at the interface.

4:40pm **DI-MoA9 Interface Band Alignment in High-k Gate Stacks***, **P. Hartlieb**, E. Bersch,* Rutgers University*; S. Sayan,* National Institute of Standards and Technology*; R. Bartynski, E. Garfunkel,* Rutgers University

Understanding and controlling band alignment remains a key aspect that must be realized if novel materials are to be incorporated in future nano-electronic devices. Photoemission, inverse photoemission, internal photoemission, and complementary methods have been used to examine (i) amorphous high-K gate dielectrics and their interface on Si, (ii) metal-oxide interfaces, and (iii) multilayered gate stacks that include metal gates and high-K dielectrics. Materials changes occur at the various interfaces during growth and processing that strongly effect device properties including the band alignment. The potential changes (effective work function) across the films have been examined as a function of material, thickness and processing ambient. Experimental results are compared to theoretical calculations to better understand the electronic properties of the different crystalline structures. It is found that the band gap, barrier height and dielectric response of this class of materials are very phase-dependent. Inverse photoemission measurements show that the conduction band shifts to higher energy going from HfO@sub 2@ to HfSiO with increasing SiO content. In contrast, addition of nitrogen shifts the conduction band to lower energy. The conduction band edge of HfO@sub 2@ rapidly shifts to lower energy upon Al metallization @footnote 1@. @FootnoteText@ @footnote 1@ The SRC, iSematech, and NSF are gratefully acknowledged for their financial support.

5:00pm **DI-MoA10 A New Approach to the Synthesis of Zr Oxynitride Alloys: Chemical and Electrical Characterizations***, **B. Ju,** G. Lucovsky,* NC State University

In order to suppress chemical phase separation in Zr silicate alloys, (ZrO@sub 2@)@sub x@(SiO@sub 2@)@sub 1-x@, at temperatures up 900°C, N-atoms have been incorporated into these alloy films by a remote plasma assisted process. Our studies indicated that N-atoms were not incorporated uniformly by this plasma process. This paper provides an alternative synthesis route that produces uniform N-atom incorporation, and also prevents formation of O-N bonds that are observed in the plasma modified Zr silicate films. In this study, Zr-Si oxynitride [(ZrO@sub 2@)@sub x@(Si@sub 3@N@sub 4@)@sub y@(SiO@sub 2@)@sub z@], x+y+z = 1, pseudo-ternary alloy films have deposited on Si (100) wafers by low temperature (300°C) remote plasma enhanced chemical vapor deposition (RPECVD). Film compositions were determined by Rutherford back scattering (RBS) and these were used to calibrate on-line Auger electron spectroscopy (AES). In general, the ZrO@sub 2@ concentration could be held relatively constant for SiO@sub 2@ rich alloys, y < z, but decreased in the Si@sub 3@N@sub 4@ rich alloy regime in which y > z. The local bonding of Zr-, Si-, O- and N-atoms in as-deposited, and annealed Zr-Si oxynitride alloys were investigated by x-ray photoemission spectroscopy (XPS) as a function of alloy composition. Previous studies have indicated that changes in the O-atom 1s core level feature provided a way to detect chemical phase separation. In alloys with up to 20 % ZrO@sub 2@ fraction, no chemical phase separation or compositional changes were detected after rapid thermal annealing (RTA) up to 1100°C in Ar for 1 minute. Capacitance-voltage (C-V) and leakage-voltage (J-V) studies were performed on metal-oxide-semiconductor (MOS) capacitors fabricated on both n-type and p-type Si substrates, and these results will be presented in the paper.

MEMS and NEMS

Room 213C - Session MN-MoA

Micro and Nano Fabrication Techniques for MEMS and NEMS

Moderator: S. Tatic-Lucic, Lehigh University

2:00pm **MN-MoA1 Parylene and Its MEMS Applications***, **Y.-C. Tai,*** California Institute of Technology **INVITED**

Parylene is the generic name for members of a unique family of thermoplastic polymers that are deposited by using the dimer of para-xylyene (di-para-xylylene, or DPXN). It is first commercialized by the Union Carbide Corporation as early as in 1956, but even today its use has been mainly limited to protective coatings of electronic components, medical instruments. Recently, however, parylene has become an emerging polymer MEMS material for various applications. This paper then reviews the related parylene MEMS technologies, material properties, and applications that were done in our Caltech lab. First, parylene is widely available through a unique room-temperature, pinhole-free, and conformal CVD deposition method, originally developed by William F. Gorham in 1950s. This benign parylene preparation process makes it a suitable technology for post-CMOS integration. Material wise, parylene has rather low melting temperature around 300 C, but it is rather inert and biocompatible. More importantly, we have shown that it is straightforward to make parylene thin film with a tensile intrinsic stress by controlling the last thermal steps. This feature allows free-standing parylene MEMS structures in many designs. As a result, we have successfully developed a multi-layer parylene MEMS technology including buried metal layers. For the last few years, we then have demonstrated various parylene MEMS applications including microstructures, micro sensors and actuators. In this paper, we will discuss parylene-based filters, neurocages, flow sensors, pressure sensors, accelerometers, bolometers, valves, pumps, etc. However, it is our belief that the brightest future of parylene MEMS is for fully integrated systems that can perform complex functions such as our on-going projects like retinal implants and labs on-a-chip.

2:40pm **MN-MoA3 Fabrication of Ferroelectric Nanomechanical Resonators***, **K. Son**, T. George,* Jet Propulsion Laboratory*; R.W. Fathauer, S. Bhaskar, W. Cao, S. Dey, L. Wang, S.M. Phillips,* Arizona State University*; B. Lambert, D.P. Weitekamp,* California Institute of Technology*; B.H. Houston, J.F. Vignola, J.E. Butler,* Naval Research Laboratory*; J. Yang, M.A. Khan,* University of South Carolina

Due to their ultra-small volumes, high sensitivity, and high operating frequencies, nano-mechanical resonators are promising for a variety of applications, including the detection of chemical or biological molecules and RF communications. A major challenge in this technology is efficient coupling to the resonator motion, particularly for applications that preclude low temperatures and/or bulky hardware. We report on our unique approach to this problem, namely the use of a ferroelectric on the resonator. Torsional geometries are used because they are amenable to our coupling technique, whereby an RF voltage applied to metal plates flanking the resonator exerts a torque on the ferroelectric. Due to its large spontaneous polarization, we are using lead zirconate titanate (PZT) as the ferroelectric. PZT is grown on both nanocrystalline diamond and single-crystal GaN resonators using the sol-gel method or MOCVD. Bare Si resonators are also being studied to provide a baseline. Novel double-paddle designs have been developed in which the paddles are supported at nodes of the motion to minimize losses through the supporting members. Their performance is compared to more conventional single-paddle designs. For resonance frequencies in the range of 0.1 to 1.0 GHz, we are examining structures with support-beam cross sections of 200 nm x 200 nm. Resonators are fabricated using electron beam lithography followed by various reactive ion etching methods specifically developed for each material. The sacrificial layers are silicon oxide for both Si and diamond resonators. For GaN, a p-type layer is used for the resonator and an n-type layer for the sacrificial layer. This allows release of the resonators using photoelectrochemical etching. Evaluation of resonators is carried out using scanning laser Doppler vibrometry, and compared to numerical simulations of resonator performance developed using finite element-based structural dynamics codes.

3:00pm **MN-MoA4 BCB-Based Linear Micromotor Supported on Microball Bearings: Design Concepts, Characterization, and Fabrication Development*, A. Modafe,*** *N. Ghalichechian, R. Ghodssi,* University of Maryland, College Park

We report on design, characterization, and fabrication development of a linear variable-capacitance micromotor (VCM) supported on microball bearings for micropositioning. Microball bearings provide robustness, stability, uniform air gap, and low friction. The stator of the VCM integrates benzocyclobutene (BCB) low-k polymer as the insulating layer with silicon micromachined V-grooves as the microballs housing. BCB polymers enable the development of MEMS-based electric machines with minimal electrical energy loss for low-temperature (<350°C) applications. We have performed an extensive characterization of electrical properties of BCB and developed a fabrication method for integration of silicon microball bearings etched in potassium hydroxide (KOH) solution with BCB insulating dielectric films. The VCM is designed to provide an aligning force of over 1 mN when driven by a 100 V square-wave excitation voltage. The electrical performance of the VCM is directly affected by the properties of BCB film. We have shown that the parasitic capacitance of the stator can be reduced by 40 % when using BCB instead of conventional oxide dielectrics. Furthermore, our capacitance tests show that the low dielectric constant of BCB does not change appreciably despite the moisture absorption in BCB; however, the current-voltage tests confirm that the breakdown strength of BCB reduces to less than half and the leakage current is doubled after moisture absorption, suggesting an upper limit for the excitation voltage. A novel fabrication process is developed to fabricate the stator V-grooves in KOH solution following the fabrication of the active area. A combination of surface treatment and cure management of BCB was used to improve the adhesion of BCB and thin film chromium/gold etch mask. Deep V-grooves as long as 20 mm were successfully fabricated in presence of BCB film. We will present the design and preliminary results of fabrication and characterization of the device.

3:20pm **MN-MoA5 Dielectrophoretic Assembly and Integration of Functional Nanodevices with VLSI Circuitry*, S. Evoy,*** *Y. Dan,* The University of Pennsylvania*; A. Narayanan, S. Raman,* Virginia Tech

The bottom-up synthesis and integration of nanoscale structures open new opportunities for the development of functional integrated systems with respect to reduced size, power consumption, and increased range of materials and functionalities that can be accessed. We present a novel platform for the development and deployment of nanosensors in integrated systems. The nanosensor technology is based on cylindrical structures grown using porous membranes as templates.@footnote 1@ These nanostructures are manipulated using dielectrophoretic forces, allowing their individual assembly and characterization. The assembly and electromechanical characterization of Rh rods and carbon nanopipes (MWNT) was performed. In addition, these segmented growth technologies have already allowed the development of striped nanowires consisting of a central functional segment terminated by two metallic extremities. @footnote 2@ Further development of such gold-terminated structures would allow assembly of sensing devices in which the metal/metal contact point would represent a negligible contribution compared to the chemresistive response of the central segment. We also report on the successful integration of nanodevices with mixed mode circuitry fabricated in a 0.18 um BiCMOS process. We were successfully able to assemble Rh nanorods of approximately 5 um in length onto prefabricated a CMOS Wheatsone bridge circuitry. We report on the designs of such mixed mode systems whose layouts integrate dielectrophoretic assembly sites with a resistance read-out, signal processing, and wireless communication circuitries. @FootnoteText@ @footnote 1@ S. Evoy, B. Hailer, M. Duemling, W. Barnhart, S. Raman, B. R. Martin, T E. Mallouk, I Kratochvilova, and T. S. Mayer, MRS Symp. Proc., 687, 63-68 (2002). @footnote 2@ S. Evoy, et al , "Dielectrophoretic assembly and integration of functional nanostructures with CMOS operating circuitry", Micro. Eng. (in press).

3:40pm **MN-MoA6 Nanoscale Synthesis of Particles and Vesicles in Microfluidic Devices*, A.P. Lee,*** University of California at Irvine **INVITED**

This presentation will focus on the development of microscale and nanoscale platform technologies for the interrogation and manipulation of biological and physiological activities. One platform we are developing can generate micro and nanoscale droplets/particles/vesicles by controlling amphiphilic interfaces in microfluidic devices. In contrast to what has currently been done, we devise new techniques and platforms for forming each individual vesicle with complete nanoscale control of parameters in order to "program" its size, shape, compositional structure, and ultimately its functions and properties. This control is enabled by nanoscale control of interfacial forces through the development of novel microfluidic technology to manipulate oil-water interfaces. These self-assembly forces are ubiquitous in nature and are responsible for the complex nanoscale structures in biological components. Through the design of microfluidic channel networks, droplet arrays present a novel method for controlling biochemistry and self-assembly at picoliter to femtoliter volumes, approaching the level of cellular activities. Nanoscale features can be designed into these vesicles that mimic biological functions such as molecular recognition, protein synthesis, and molecular transport. Based on the materials delivered, droplets can then form polymer nanoparticles (e.g. photopolymerization), lipid bilayer vesicles, and multilayer drug particles. Applications that we are pursuing include smart vesicles for targeted imaging and therapeutics for cardiovascular diseases, synthetic antibodies by molecular imprint polymer nanoparticles, protein crystallization, quantum dot synthesis in droplet microreactors, combinatorial cell-based assays, and cell-encapsulation for combinatorial assays and tissue engineering.

4:20pm **MN-MoA8 Layered Nanofabrication (lnf) As a Tool for NEMS and Bio-NEMS*, B.E. Koel,*** *A.A.G. Requicha, M.E. Thompson,* University of Southern California

We have proposed a new rapid prototyping technique at the nanoscale, called Layered Nanofabrication (LNF)@footnote 1@. A nanometer-sized, three-dimensional (3-D) object can be build by successive fabrication of layers in which nanoparticles are first deposited and then manipulated by using atomic force microscopy (AFM). Each layer is then planarized by adding a molecular sacrificial layer whose top surface serves as a support for the next processing step. The sacrificial layers, or conversely the nanoparticles, are removed in a final step. Achieving suitable planarization for LNF requires extreme constraints on the approach used for this process. We have focused thus far on pushing the efficiency and control in deposition of films from self-assembled monolayers (SAMS). Improvements in permanently bonding or linking nanoscale components are also required. Our progress to date will be reviewed, including discussion of various siloxane and other SAMS, and chemical linking of and electrochemical deposition on Au nanoparticles. @FootnoteText@ @footnote 1@A. A. G. Requicha, S. Meltzer, R. Resch, D. Lewis, B. E. Koel, and M. E. Thompson, Layered nanoassembly of three-dimensional structures, Proc. IEEE International Conf. on Robotics & Automation, Seoul, S. Korea, pp. 3408-3411, May 21-26, 2001.

4:40pm **MN-MoA9 Ultrafast Fabrication of 3D Microstructures for MEMS Applications*, H. Yu,*** Boston University, US*; B. Li, X. Zhang,* Boston University

Recently, the interest in three-dimensional (3D) microstructures with mechanical, electrical, optical, and biological functionalities has increased dramatically. These microstructures promise to be of great importance for numerous applications including those for the coming biotechnology revolution. This paper introduces an innovative 3D fabrication method by using a laser scanning system, which allows for rapid processing of freeform multi-layered microstructures, and more importantly enables fast development of microdevices with a low cost. In particular, by using this method, we can create a variety of 3D microstructures including: oblique micropillar arrays, micro T-plugs, embedded microchannels, and freestanding microcantilevers. Compared to the existing manufacturing techniques, our direct UV laser writing method greatly simplifies fabrication processes, potentially reducing the design-to-fabrication time to a few hours. Furthermore, the process can be set up in a conventional manufacturing environment without the need for clean room facilities. The ultrafast and low cost characteristics allow our method to be extremely beneficial during the product development stages. The initial process validation has been presented by using SU-8 material. This technique is expected to be able to process a broad range of materials, including polymers, metals, and semiconductors by using ultrafast lasers. The results presented in this paper serve as the first crucial step towards the rapid manufacturing of microdevices with mechanical, optical, and/or biological functionalities for enormous applications.

5:00pm **MN-MoA10 Micro-fabricated Charge-sensing Resistive Probe*, H. Park*,** *J. Jung, D.-K. Min, C. Park, K. Baeck, S. Kim, H. Ko, S. Hong,* Samsung Advanced Institute of Technology, Korea

We fabricated a scanning probe microscopy (SPM) probe that can image surface charges of ferroelectric domains at high speed without an additional signal modulation system like a lock-in amplifier. The probe detects electric field by field-induced resistance change in a semiconductor resistive region formed at the apex of the tip; the majority carriers in the resistive region are depleted or accumulated by the electric field. To minimize the size of the resistive region and align it at the apex of the tip, we developed a self-aligning process, which is designed to etch Silicon for tip formation with the same masking material as that used in the preceding ion implant process forming the resistive region. We simulated tip fabrication process using SUPREM IV and confirmed that only low-doped n-type resistive region of 150 nm size existed at the tip apex as designed. In order to measure the field sensitivity, we contacted the fabricated resistive probe on a thermally oxidized silicon sample and measured 0.5 % resistance change per voltage applied to the sample. The response time to the external field was about 10 nsec. We obtained domain images of triglycine sulfate (TGS) single crystal with the probe in contact mode. The operating voltage of the probe was 2 V and the scan rate was 2 Hz. We controlled the polarization of Pb(Zr@sub 0.4@Ti@sub 0.6@)O@sub 3@ (PZT) by applying voltage between the resistive tip and the bottom electrode of PZT, and acquired the domain images with the same probe at 2 Hz scan rate. The diameter of detected domain was 500 nm and the transition width between opposite domain images was about 120 nm. By controlling and detecting the ferroelectric domains without an additional signal modulating system, we verified that the resistive probe could be used for a high speed SPM mapping surface charges and be applied to the probe-based data storage system in which a fast read/write head of simple structure and process is essential.

Nanometer-scale Science and Technology
Room 213D - Session NS-MoA

Magnetic Imaging and Spectroscopy

Moderator: B.D. Terris, Hitachi Global Storage Technologies

2:00pm **NS-MoA1 Spin-Polarized Scanning Tunneling Microscopy: Achievements and Perspectives*, M. Bode*,** *K. Von Bergmann, O. Pietzsch, A. Kubetzka, R. Wiesendanger,* University of Hamburg, Germany **INVITED**

Within the past decade spin-polarized scanning tunneling microscopy (SP-STM) was developed to a mature technique which not only allows for ultra-high spatial resolution studies of magnetic nanostructures, but also enables the direct correation with the sample`s topography and spin-resolved electronic structure. By reviewing the main achievements of SP-STM, which include the observation of size-dependent reorientation transitions @footnote 1@, the impact of strong external fields on magnetic nanowires @footnote 2@, atomic resolution of antiferromagnetic monolayers @footnote 3@, and the direct observation of thermal switching events of indivitual superparamagnetic entities @footnote 4@, we will discuss the strength and limitations of the technique. Possible future developments will be sketched and evaluated. @FootnoteText@ @footnote 1@ A. Kubetzka et al., Phys. Rev. B 63, 140407 (2001). @footnote 2@ O. Pietzsch et al., Science 292, 2053 (2001). @footnote 3@ S. Heinze et al., Science 288, 1805 (2000). @footnote 4@ M. Bode et al., Phys. Rev. Lett. 067201 (2004).

2:40pm **NS-MoA3 Atomic-Scale Spin-Polarized Scanning Tunneling Microscopy of Magnetic Transition Metal Nitride Surfaces*, A.R. Smith*,** *R. Yang,* Ohio University*; H.Q. Yang,* Texas A&M University*; W.R.L. Lambrecht,* Case Western Reserve University*; A. Dick, J. Neugebauer,* Fritz-Haber-Institut der MPG, Germany **INVITED**

Spin-polarized scanning tunneling microscopy (SP-STM) can achieve ultimate magnetic resolution on surfaces, even down to the atomic scale.@footnote 1@@footnote ,@@footnote 2@@footnote ,@@footnote 3@ In earlier work, we have shown the resolution of the spin structure of a novel antiferromagnetic (aFM) surface, Mn@sub 3@N@sub 2@ (010), with a model row-wise aFM structure.@footnote 3@ The surface is prepared using molecular beam epitaxy with a Mn effusion cell and radio frequency N plasma. The magnetic information appears as an additional component which is added to the non-magnetic component in the STM line scan. Furthermore, the magnetic information is bias-dependent; both the amplitude and polarity of the magnetic profile vary with the STM bias. The bias-dependence is understood as energy-dependent variations of the spin density of states of tip and sample. Both the magnetic and non-magnetic information can be extracted from the total STM image and compared with simulations based on theoretical calculations. Using first principles density functional theory, the local density of states for the surface is calculated for Mn@sub 3@N@sub 2@ (010). Two methods of simulation have been investigated for SP-STM. First, we have applied the atom superposition method (ASM). Second, we have simulated the images using the full Tersoff-Hamann (T-H) approach.@footnote 4@ We find that the T-H method is, in general, necessary for a correct simulation of the data due to the spin-dependent orbital lobes of the surface atoms. We furthermore apply the full T-H theory with different numbers of tip atoms to best model the STM data with good success. @FootnoteText@ @footnote 1@S. Heinze {\it et al.}, Science {\bf 288}, 1805 (2000). @footnote 2@D. Wortmann {\it et al.}, Phys. Rev. Lett. {\bf 86}, 4132 (2001). @footnote 3@H. Yang {\it et al.}, Phys. Rev. Lett. {\bf 89}, 226101 (2002). @footnote 4@J. Tersoff et al., Phys. Rev. Lett 50(25), 1998 (1983).

3:20pm **NS-MoA5 Spin-Polarized Scanning Tunneling Microscopy Study of Single-Crystallized Nanodot Arrays*, T.-H. Kim*,** Seoul National University, South Korea, S. Korea*; J.H. Choi, J. Seo, Y. Kuk,* Seoul National University, South Korea

We have developed a method to grow regularly patterned Fe nanodot arrays with in situ deposition. A self-sustained porous alumina mask was fabricated with an aluminum-coated Si substrate. Using the alumina shadow mask with perfectly ordered pores, we fabricated well-ordered Fe nanodot arrays.@footnote 1@ Fe nanodot arrays with 0.2-10 nm thicknesses, 50-120 nm diameters, and 100-200 nm periods were successfully grown on a W(110) substrate in ultra-high vacuum. Fe nanodots were single-crystallized by mild annealing. Our shadow mask technique can be the simple and fast method to obtain high-density arrays over a macroscopic area. Spin-polarized scanning tunneling microscopy (SP-STM), one of the most powerful techniques to study magnetic nanostructures, can image surface domain structures with a lateral resolution reaching the atomic scale.@footnote 2@ Well-ordered Fe nanodot arrays showed a stronger magnetic interaction between dots than randomly distributed Fe islands. We have performed micromagnetic simulation@footnote 3@ to study interaction between dots. @FootnoteText@ @footnote 1@ J. H. Choi, T.-H. Kim, J. Seo, and Y. Kuk (submitted to APL).@footnote 2@ S. Heinze, M. Bode, A. Kubetzka, O. Pietzsch, X. Nie, S. Blugel, and R. Wiesendanger, Science 288, 1805 (2000).@footnote 3@ We used the OOMMF program (http://math.nist.gov/oommf/). .

3:40pm **NS-MoA6 Spin-Resolved Core Level Photoemission of Ferromagnetic Thin Films*, G.D. Waddill*,** *T. Komesu,* University of Missouri-Rolla*; S.A. Morton,* Lawrence Berkeley National Laboratory*; J.G. Tobin,* Lawrence Livermore National Laboratory

We present spin-resolved 2p core level photoemission results for thin films of Fe, Co, and Ni. The films are bcc Fe on a Ag(100) substrate, fcc Co on Cu(001), and fcc Ni/Co/Cu(001). All films have an in-plane magnetic easy axis. We observe spin polarization in the main photoemission peaks consistent with trends in the bulk magnetic moments of the transition metals. In addition, Ni and Co have satellite peaks due to electron correlation effects and we see spin polarization in the Ni 6 eV satellite peak and much weaker spin polarization in the 4 eV Co peak. The existence of a satellite peak in the Co 2p spectrum is somewhat controversial and this data marks the first observation of spin-polarization in that peak. In addition, in the Ni/Co/Cu(001) system we have preliminary results for very thin films of Ni where charge transfer from the Co to the Ni will effect the electronic and magnetic properties of both films. For a 3 monolayer Ni film on Co we see differences in the photoelectron spin polarization of both Co and Ni compared to results for thicker Ni and Co films. These results emphasize the importance of spin-resolved photoemission in understanding the combined Coulomb, spin-orbit, and exchange interactions in the presence of interatomic electron correlation effects and configuration mixing that effect the photoemission process.

4:00pm **NS-MoA7 Spin Polarized Electron Energy Loss Spectroscopy on Ferromagnetic Thin Films*, T. Komesu*,** *G.D. Waddill,* University of Missouri-Rolla*; J.G. Tobin,* Lawrence Livermore National Laboratory

Spin-polarized electron energy loss spectroscopy (SPEELS) developed in the 1980s and has become a valuable technique for probing Stoner excitations and spin waves. SPEELS is sensitive to the occupied and unoccupied parts of the spin-split electronic structure of materials, and consequently SPEELS is a complementary technique to spin-resolved photoemission and inverse photoemission that more directly probe the occupied and unoccupied spin-split band structure respectively. Our results, using an unpolarized electron source with spin analysis shows sharp spin-dependent energy loss features in electron scattering from ferromagnetic thin films of Fe, Ni, and Co grown on Ag(100) and Cu(001). This is in contrast to most previous SPEELS studies (primarily using spin-polarized sources and spin analysis) where very broad featureless spectra are observed. We attribute the majority spin peaks we observe to spin-flip exchange scattering from the magnetic films, with the lowest energy feature corresponding to the exchange splitting for the films. The observed minority spin peaks are attributed non-flip exchange scattering.

4:20pm **NS-MoA8 High-Resolution Imaging of Magnetization Dynamics Using X-PEEM*, A. Scholl,*** Lawrence Berkeley National Laboratory **INVITED**

Ultrafast x-ray pulses (p-sec to f-sec) promise to be an ideal tool to probe the dynamics of magnetic materials. X-rays are sensitive to both ferromagnetic and antiferromagnetic order. Sum rules allow us to quantify spin moment, orbital moment and magnetic anisotropy specific for each element in a sample. High spatial resolution on the order of nanometers can be obtained using x-ray microscopy techniques using zone-plates or electron microscopes. As an example, a study of the precessional dynamics of magnetic vortices, 3-dimensional magnetic curls, will be presented [1]. The dynamics is probed at 100 nm spatial resolution and 70 ps temporal resolution using the PEEM-2 Photoemission Electron Microscope at the Advanced Light Source. It will be demonstrated that the vortex chirality or handedness, which is determined by the out-of-plane magnetization of the vortex core, governs the sub-ns dynamics of the structure, leading to a precessional motion of the vortex center. The dynamics is initiated by a sub-ns field pulse triggered by a laser, which is synchronized to the x-ray source. In contrast, on longer time scales it is known that damping dominates and the dynamics is governed by the in-plane domain structure. The measured vortex speed and the internal magnetic field at the core will be compared with the result of micromagnetic simulations and with the static susceptibility of the magnetic structure. The potential of studying processes beyond the Landau-Lifshitz-Gilbert dynamics using currently developed ultrafast x-ray techniques will also be discussed. [1] S.B. Choe et al., Science 304, 420 (2004).

5:00pm **NS-MoA10 Magnetic Interaction between a Ferromagnetic Substrate and Adsorbed Manganese Porphyrin Molecules***, A. Scheybal,* ***T. Ramsvik,*** Paul Scherrer Institute, Switzerland*; R. Bertschinger,* Paul Scherrer Institut, Switzerland*; M. Putero-Vuaroqueaux,* L2MP-CNRS, France*; T.A. Jung,* Paul Scherrer Institute, Switzerland

The magnetic interaction between a magnetized thin film cobalt substrate and adsorbed manganese(III)-tetraphenylporphyrin chloride (MnTPPCl) molecules has been studied using X-ray magnetic circular dichroism (XMCD). In the regime of submonolayer coverage a clear circular dichroism is observed at the Mn L@sub 32@-edge, verifying that a net magnetization is set up by the manganese ions in the adsorbed molecules. An element specific hysteresis study shows that the magnetic properties of the molecules mirror those of the cobalt substrate. From this and from temperature dependent studies it is concluded that exchange interaction between the cobalt film and the molecules is the dominant cause for this induced magnetism. To our knowledge, this is the first time that an exchange coupling between adsorbed organic molecules and a ferromagnetic substrate has been demonstrated by XMCD at 3d-transition metal L@sub 32@-edges, thereby allowing direct information about both orbital and spin magnetic moments@footnote 1@. As MnTPPCl is the parent compound of the [Mn(III)-porphyrin][TCNE] family of molecular magnets (TCNE = tetracyanoethylene)@footnote 2@, the here presented molecular system and experiment provides a model system for the study of the magnetic interaction at the interface between a conventional ferromagnet and a molecular magnet. Furthermore, an organic semiconductor like tris(8-hydroxyquinoline) aluminium (Alq@sub 3@) can be used to prepare an organic spin-valve exhibiting giant magnetoresistance, as it has been demonstrated recently.@footnote 3@ Thus, the understanding of local magnetic coupling in molecular materials is of utmost importance for the application of magnetic materials in ever smaller dimensions. @FootnoteText@ @footnote 1@ G. Schütz et al., Phys. Rev. Lett. 58 (1987) 737@footnote 2@ J.S. Miller et al., Adv. Mat. 4 (1992) 498@footnote 3@ Z.H. Xiong et al., Nature 427 (2004) 821.

Plasma Science and Technology
Room 213A - Session PS1-MoA

Plasma Surface Interactions in Etching

Moderator: M.C.M. van de Sanden, Eindhoven University of Technology, The Netherlands

2:00pm **PS1-MoA1 Quantitative Plasma Beam Investigation of Polysilicon Sidewall Roughening*, S.A. Rasgon*[1]***, Y. Yin, H.H. Sawin,* Massachusetts Institute of Technology

For the patterning of sub 100 nm features,a clear understanding of the origin and control of line edge roughness (LER) is extremely desirable, particularly at the gate level where variations in line width can adversely impact the electrical performance of the device. Plasma etching processes often roughen the feature sidewalls, leading to the formation of anisotropic striations. It is this post-etch sidewall roughness which will ultimately affect device performance. Our past research has focused on the observation of sidewall roughness via a novel AFM technique. The resulting images allow the extraction of quantitative information on sidewall roughness and spatial frequency as a function of depth, and vividly highlight the structure of the post-etch sidewall. While these images present a remarkable display of sidewall roughness encountered in common etching processes, a fundamental study of post-etch sidewall roughness remains elusive due to the inherent experimental difficulties encountered. Sidewall roughening during etching depends on the plasma chemistry, ion bombardment energy, and ion incident angle. A true fundamental study requires independent control of all three parameters, impossible to obtain in a conventional plasma etcher. To remedy these difficulties, an inductively-coupled plasma beam source was constructed that allows the exposure of a sample to a realistic ion and neutral flux, of any desired plasma chemistry, while allowing independent control of the ion bombardment energy and incident angle. By rotating the sample to a near-glancing angle, a sidewall can be simulated. This apparatus is used to conduct a fundamental study of sidewall roughness/striation during HBr etching of polysilicon. The resulting AFM images are analyzed for roughness magnitude/spatial frequency using a novel geostatistical technique, and are compared with real sidewalls. Finally, insight into the roughening mechanism is obtained through 3D modeling of the roughening process.

2:20pm **PS1-MoA2 3-Dimensional Feature Scale Simulation of Polysilicon Sidewall Roughening*, H. Kawai,*** *W. Jin, H.H. Sawin,* MIT

The line edge roughening has become an important factor as the features shrink. Although there are 2-dimensional simulators that can simulate the artifacts such as faceting and microtrenching, they can not simulate the surface roughness since it is inherently 3-D in nature. Therefore, a 3-dimensional simulator was developed to study the physics of surface and line edge roughening. 2 Â½ -dimensional simulator, that had been developed before, applied Monte Carlo model to model the surface kinetics. Although 3-D simulator also used Monte Carlo model, many changes were made to convert the simulator from 2 Â½ -D to 3-D. These include a new algorithm for the computation of surface normals and fluxes on sidewalls. In addition, since 3-D simulator is more computationally intensive, it is necessary to optimize the simulator by minimizing the computation time while maintaining the accurate results. Simulation domain was discretized into cubic cells with the side of 2.5 nm, and when a particle strikes a surface cell, the local surface conformation was determined. The algorithm was based the fitting of the local region of the surface cells with a polynomial. The cell size of 2.5 nm had been used since the cell size corresponds to the ion induced mixing length. Since the grooved striations formed in line edge roughening have minimum radius of curvatures of about 25 nm, the appropriate degree of polynomial and number of cells to be fitted were selected to allow the representation of surface curvatures of 25 nm or less. This fitted surface is then used to compute the surface normal, scattering angle, and flux on the 3-D surface. The surface normal was used to determine the movement of the surface with material etching or deposition by selecting the appropriate cell for cell addition or collapse.

2:40pm **PS1-MoA3 Unraveling the Complex Process Known as 'Plasma Chemistry'*, M.J. Goeckner,*** University of Texas at Dallas **INVITED**

'Plasma chemistry' is perhaps one of the most complex processes known. In general it can be thought of as the interaction between three main scientific subsystem, plasma physics, gas-phase chemistry/physics and

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

surface-phase chemistry/physics. To understand this complexity one simply needs to consider how a given reactive gas-phase specie might interact with a surface. Does it stick to the surface? Does it chemically react with the surface? Does it promote film growth? How does this interaction change the gas composition? How does an altered gas-phase chemistry alter the plasma? Understanding these interactions is key to producing better models of plasmas, allowing the optimization of complete process systems and hence improved product yield. This talk will briefly review how various groups are attacking this complex problem. Then using our fluorocarbon chemistries (CF@sub 4@, C@sub 4@F@sub 8@) studies as an example, we examine how gas and surface chemistries change for different wall conditions (temperature, diameter and material) as well as gas flows and plasma parameters. Based on this knowledge, we will discuss possible interaction mechanisms and how these might affect the process. This will in turn lead to a discussion of possible future studies. This work is supported by a grant from NSF/DOE, CTS-0078669.

3:20pm **PS1-MoA5 Stabilization of Radical Composition Drift in Fluorocarbon Plasmas***, **K. Nakamura**,* Chubu University, Japan*; H. Sugai,* Nagoya University, Japan*; K. Oshima, A. Ando, 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 a RF bias to the chamber wall@footnote 1@. This paper reports the effects of the AIB on polymer film deposition onto the chamber walls and the time-variation of radical density in fluorocarbon plasma reactors. 13.56 MHz inductively-coupled plasmas are 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. The AIB drastically suppressed polymer deposition on the biased wall, and the deposition rate decreases by one order of magnitude with ~100 eV ion bombardment compared to the non-bias case. On the other hand, the AIB also reduces a rise time of densities of the fluorocarbon radicals after the discharge starts, and reached to steady state within ~10 s for CF@sub 2@ radicals. @FootnoteText@ @footnote 1@K. Nakamura et al: J. Vac. Sci. Techonol. A 18 (2000) 137.

3:40pm **PS1-MoA6 Etching of Passivated SiO@sub 2@ Film by Fluorocarbon Ions: A Molecular Dynamics Study***, V. Smirnov, A. Stengatch, **V. Pavlovsky**,* Sarov Labs., Russia*; S. Rauf, P. Stout, P.L.G. Ventzek,* Freescale Semiconductor

Fluorocarbon plasmas are widely used for etching of dielectric thin films in the microelectronics industry. Fluorocarbon radicals and ions are known to produce a thin passivation layer (~ 2 nm) 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 dielectric etching. Computational molecular dynamics (MD) is one technique that has proven useful for such studies. This paper reports about a MD based investigation of fluorocarbon passivated SiO@sub 2@ film etching by CF@sub x@ (x=1, 2, 3) ions. Our MD code is 3-dimensional and uses the velocity-Verlet method for particle acceleration. Psuodo-potentials for two and three body interactions of Si, O, C, and F have been assembled either using Gaussian based quantum chemistry computations or data available in literature. A variety of fluorocarbon passivation films (with varying thickness and F/C ratio) are prepared by bombarding low to medium energy fluorocarbon ions on SiO@sub 2@. Impact of energetic (50-1000 eV) CF@sub x@ ions on these passivation films is then investigated, and modeling results are used to determine ion etch yield, nature of sputtered clusters, and their energy and angular distributions. Modeling results clearly demonstrate that presence of a fluorocarbon passivation film enhances etch yield compared to a similar but otherwise unpassivated SiO@sub 2@ film. Etch yields peak at an off-normal angle, and SiO@sub x@F@sub y@ constitute the bulk of Si containing sputtered clusters.

4:00pm **PS1-MoA7 Spontaneous Etching of Silicon with F Atoms and XeF@sub 2@: A Unified Model***, **H.F. Winters**, D. Humbird, D.B. Graves,* UC Berkeley

A recently proposed molecular dynamics simulation of spontaneous etching of undoped silicon with F has been successful in describing a variety of experimental observations.@super 1@ Insights gained from this simulation (denoted HG) have been used to refine a model which explains other spontaneous etch observations, including etching by XeF@sub 2@ and various effects of doping on spontaneous etching, among others. The model is based on the assumption that the reaction is proportional to the negative ion concentration on the silicon surface (e.g. at SiF@sub 3@@super -@ centers)@super 2@ using the umbrella-type reaction mechanism observed in the simulation. HG predicts a 5 Å SiF@sub x@ layer on silicon exposed to F atoms and it will be demonstrated that XPS data are consistent with this prediction. It will also be shown that XPS data indicate a layer twice as thick (~10 Å) for XeF@sub 2@. Experimental data showing that the layer thickness is relatively independent of incident flux and temperature over significant ranges of these parameters as predicted by HG will be presented. Assuming these layer thicknesses are correct allows us to calculate the negative ion concentration on the silicon surface being etched.@super 2@ These results are correlated with various experiments including reaction probability measurements over the temperature range 200--1000 K and doping experiments with concentrations from ~10@super 15@ to 10@super 20@ dopants/cm@super3@. It will be shown that one model can be used to describe the experimental results for the spontaneous etching of Si(111) by both F and XeF@sub 2@. A plausible explanation will be presented as to why the doping effect in chlorine is large relative to fluorine even though the opposite trend is observed for spontaneous etch rate. Many other experimental results (etch rate proportional to reactant density, insensitivity of product distribution to doping level, etch product composition, and the doping and reaction probability differences between F and XeF@sub 2@) are consistent with this model. Finally, the HG conclusion that etch products are desorbed with significant kinetic energy allows data from modulated beam mass spectrometry calibrated for 300K products to be interpreted properly, leading to determination of the reaction probability from T(surface) = 200 K - 1000 K. The data will be presented and compared with theory. @FootnoteText@@Footnote 1@ David Humbird and David B. Graves, J. Appl. Phys, in press, (2004) @Footnote 2@ H. F. Winters and D. Haarer, Phys.Rev. B, 36. 6613 (1987); 37 ,10379 (1988)

4:20pm **PS1-MoA8 Real-time Spectroscopic Studies of Si Etch Dynamics***, **A.A.E. Stevens**, J.J.H. Gielis, M.C.M. van de Sanden, H.C.W. Beijerinck, W.M.M. Kessels,* Eindhoven University of Technology, The Netherlands

Nanometer scale control during IC, MEMS/NEMS and photonic device production becomes more and more an issue. Plasma etching and ion beam processing cause the creation of surface roughness and defects, such as dangling and strained bonds. The roughness and defects resulting from the production process end up at critical interfaces in the devices and, thus, influence their performance in a negative way. Therefore, fundamental studies of the creation of roughness and dangling/strained bonds in plasma and ion beam processing of silicon are required. In the past, mass spectrometry studies in well-characterized beam-etching experiments revealed a great deal of information regarding the synergy between ions and etchant during Si etching. At present, more detailed information is desired and can be obtained with spectroscopic surface diagnostics, which have made significant advances over the last years. Hence, spectroscopic ellipsometry (SE) and second harmonic generation (SHG) are employed in situ and real-time during the etching of Si with beams of Ar@super +@ [10-2000 eV] and XeF@sub 2@. By means of SE the surface roughness is measured. If the etching is dominated by XeF@sub 2@ etching, the surface becomes rough (d@rough@ ~ 1-10 nm). However, when Ar@super +@ ions are driving the etch process, the surface remains relatively smooth (d@rough@ < ~1 nm). Complemented with atomic force microscopy measurements, the dynamic roughness scaling theory, expressed in parameters @alpha@ and @beta@, is applied to find the origin of the roughening processes during the etching. In order to study the creation of dangling and strained bonds SHG studies are being carried out. The role of the ions and etchant in the creation of roughness and defects at etched Si surfaces will be discussed on the basis of the results obtained with these surface-sensitive spectroscopic analysis techniques.

4:40pm **PS1-MoA9 Insights into the Ion Energy Dependence of Ion-Assisted Chemical Etch Rates in High-Density Plasmas**, ***L. Stafford***, *J. Margot,* Universite de Montreal, Canada; *M. Chaker,* INRS-Energie, Canada; *S.J. Pearton,* University of Florida

Over the last few years, important research efforts have been devoted to the development of plasma etching models of various materials in various reactive plasma mixtures. These models generally include a surface kinetic model in which it is usually assumed that the ion-assisted chemical etch rate varies like the square root of the ion energy. This dependence is empirically deduced from the universal energy dependence of physical and ion-assisted chemical etch yields presented by Steinbruchel.@footnote 1@ In the present work, we show from existing experimental data that the ion-assisted chemical etch rate does not necessarily follow this particular energy dependence. A typical example is provided by the etching of ZnO films in an Ar/Cl2 high-density plasma. To explain this behavior, we propose an analytical model in which the formation rate of the adsorbate is assumed to be proportional to the number of adsorption sites. In the specific case of ZnO, the adsorption sites are generated by thermal desorption of oxygen atoms. This is found to induce a non-linear relation between the etch rate and the square root of the ion energy. For oxide materials with more complicated structures like (Pb,Zr)TiO3 (PZT), ion bombardment is required to generate adsorption sites. In this case, the adsorbate formation depends on ion energy, which results in an etch rate that approximately varies like the square root of the ion energy. The predictions of our model are found to be in excellent agreement with the experimental data reported for several materials, for example ZnO, SiO2, HfO2, PZT, PST, and SBT. In addition, the model includes previous ion-assisted etching models such as that developed by Gottscho and his co-workers.@footnote 2@. @FootnoteText@ @footnote 1@ C. Steinbruchel, Appl. Phys. Lett. 55, 1960 (1989)@footnote 2@ R.A. Gottscho, C.W. Jurgensen and D.J. Vitkavage, J. Vac. Sci. Technol. B 10, 2133 (1992) .

5:00pm **PS1-MoA10 A Model of Multilayer Surface Reactions and Simulation of the Feature Profile Evolution in Etching of Silicon in Chlorine Plasmas**, ***Y. Osano***, *K. Ono,* Kyoto University, Japan

A phenomenological model has been made to simulate the feature profile evolution of nanometer-scale etching of Si in Cl@sub 2@. The model incorporates an atomistic picture into the model, to analyse the complex surface reactions in the ion-enhanced etching and investigate their effect to the profile evolution, which involves profile anomalies such as bowing, tapering, and microtrenching. To simulate the reaction process at an atomic scale, we employ a feature profile modeling with two-dimensional array of atomic size cell in the entire computational domain. Monte Carlo calculation of the trajectory and stopping of the incoming Cl@super +@ ion within the surface layers of Si substrate is then performed, on the basis of kinetics of two-body elastic collision. For surface reactions of Cl neutral reactants, we take into account their adsorption on the very surface layer. The removal of Si atom is assumed to be caused by the reaction on the chlorinated surface in terms of this adsorption process Si@sub (s)@+4Cl@sub (s)@ -> SiCl@sub 4(g)@, where (s) and (g) represent the solid and the gas, respectively. Simulation of the feature profile evolution is performed for etching of sub-100 nm patterns. The effect of neutral-to-ion flux ratio is studied in this calculation. The present model illustrates that changes of the flux ratio have a significant effect on surface anomalies, such as sidewall bowing and tapered feature near the bottom, associated with surface chlorination on the feature surface which varies by the flux ratio and the location within the feature pattern.

Plasma Science and Technology
Room 213B - Session PS2-MoA

Emerging Plasma Applications

Moderator: H. Barankova, Uppsala University, Sweden

2:00pm **PS2-MoA1 Dielectric Barrier, Atmospheric Pressure Glow Discharges (DB-APGD) : Applications, Diagnostics and Modeling**, ***M.R. Wertheimer***, *I. Radu,* Ecole Polytechnique de Montreal, Canada; *R. Bartnikas,* Hydro Quebec Research Institute, Canada **INVITED**

The field of "cold" (non-equilibrium) plasmas at atmospheric pressure (AP) is receiving much attention, in part due to the reward of more economic processing without vacuum systems. Dielectric barrier discharges (DBD) are a particularly promising subgroup; among these, AP glow discharges (APGD) occur in certain gases with long-lived energetic states, for example in N@sub2@ and in the noble gases. They manifest several remarkable peculiarities, described below, and they have opened application areas as diverse as (a) polymer surface modification, (b) deposition of novel thin film materials, (c) short wavelength light sources for photochemistry, (d) plasma displays, and numerous others. The presentation commences with a short overview of these recent industrial innovations; we then describe fundamental and applied research on DB-APGD in this laboratory. In the former category, diagnostic and modeling studies in helium are briefly presented : (i) At low applied a.c. voltage, V, a single, multi-µs current pulse per half-cycle occurs, but the "glow" may comprise many geometrically-ordered plasma columns which ignite and extinguish in perfect synchronism; (ii) at higher V, these merge into a "true" APGD, spread uniformly over the entire electrode area. (iii) Under specific conditions of V and the a.c. frequency, f, a "pseudoglow" regime sets in, comprising two or more pulses of monotonically decreasing amplitudes per half-cycle. We explain observations (i) to (iii) and demonstrate excellent agreement between experimental measurements (e.g. spatial and temporal evolution of the discharges) and the two-dimensional theoretical model developed by Novak and Bartnikas. Finally, turning to applied research, the unique capabilities of DB-APGD processing of materials is illustrated with several examples drawn from categories (a), (b) and (c) identified above.

2:40pm **PS2-MoA3 Hot Hollow Cathode Diffuse Arc Deposition of Chromium Nitride Films**, *H. Barankova,* ***L. Bardos***, *L.-E. Gustavsson,* Uppsala University, Sweden

The hollow cathode in the diffuse arc regime (arc with hot thermionic cathode) was used for deposition of chromium and chromium nitride films. The chromium hollow cathode serving as a gas inlet was connected to a radio frequency (rf) generator with the rf power up to 350 W. The process of generation and performance of the hollow cathode discharge and its transition to the arc regime was examined for different gases. The comparison is also given with other target metals. The reactive process of CrN deposition was investigated. Films were deposited on unheated silicon and steel substrates. Highly oriented crystalline CrN films were deposited at retes up to 4.5 @mu@m/min. The effect of process parameters and their correlation to properties (microcrystalline structure, hardness and deposition rate) of CrN is given.

3:00pm **PS2-MoA4 Atmospheric Plasma Deposition of Abrasion Resistant Coatings on Plastic**, ***G. Nowling***, *M. Moravej, M. Yajima, R.F. Hicks, X. Yang,* University of California, Los Angeles; *S. Babayan,* Surfx Technologies; *W. Hoffman,* Motorola

{The plasma-enhanced chemical vapor deposition of silicon dioxide on plastic has been examined in an atmospheric pressure discharge operating with 2.0 vol.% oxygen in helium, at 100 W RF power, and a gas temperature of ~100@degree@C. Several silicon precursors were studied, including tetramethyldisiloxane (TMDSO), tetramethyl-cyclotetrasiloxane (TMCTS), tetraethoxysilane (TEOS), hexamethyldisiloxane (HMDSO) and hexamethyldisilazane (HMDSN). After growth, the thickness, refractive index, composition, and structure of the films were determined by ellipsometry, infrared spectroscopy, and three-dimensional surface imaging. Hardness and abrasion tests were performed as well. Glass films could be deposited at rates up to 1.0 micron/minute using TMDSO. However, these films contained significant amounts of carbon and hydrogen, and abraded easily during scratch tests. Feeding HMDSN to the oxygen plasma resulted in the deposition of SiO@sub2@ films that were free of nitrogen and carbon, contained minimum hydroxyl concentrations, and displayed excellent hardness and scratch resistance at a film thickness >1.5 microns. The maximum deposition rate obtained using HMDSN was 0.3 microns/minute. At the meeting, we will discuss the relationship between the plasma chemistry and the properties of the glass coatings.}

3:20pm **PS2-MoA5 Plasma Surface Modification for In-line Commercial Applications**, ***A. Yializis***, *R.E. Ellwanger,* Sigma Technologies Int'l Inc. **INVITED**

Plasma is the most common state of matter in the visible universe and has been used for decades in commercially important processes. However, such processes have historically tended to be limited to fairly small scale vacuum applications. The idea of using plasma, particularly atmospheric plasma, to add substantial value to a product by modifying the surface of a moving substrate with either added functionality or a thin functional coating is indeed compelling. Emerging applications include elevation of surface energy to promote adhesion or wetability, ablation to remove unwanted residue or material, sterilization, and deposition of a thin functional coating. Sigma Technologies has been at the leading edge of efforts to commercialize these concepts for the past several years and recent results in the aforementioned application areas are presented.

4:00pm **PS2-MoA7 Fundamental Aspects on the Sputter Efficiency in High Power Pulsed Magnetron Sputtering*, U. Helmersson***, *J. Alami, J. Böhlmark, M. Lattemann,* Linköping University, Sweden

The use of high power pulsed magnetron sputtering (HPPMS) is an elegant way of producing a large amount of ions from the sputtered materials in magnetron sputtering (MS). HPPMS has great potential in thin film deposition where there is a desire to control direction, lateral distribution, and arrival energy of the depositing species. In this paper we present measurements of the deposition rate using HPPMS and comparing it with normal dc MS. It shows that in general the deposition rate is lower for HPPMS using the same average input power and that the deposition rate scales with the self-sputtering yield of the sputtered material in use. This can be understood in view of the large fraction of ionized metal in the close vicinity of the cathode and that the metal itself will be responsible for a large fraction of the effective sputter ejection of the cathode material. The observed results are also discussed in view of the pulse power and inert gas pressure used.

4:20pm **PS2-MoA8 RF Plasma Deposition of Thin SiO@subx@ Films onto Aluminium Alloy: XPS and Contact Angle Measurements Studies*, A. Azioune***, *M. Marcozzi, V. Revello, J.-J. Pireaux,* Lise Namur, Belgium

Protection of (metallic) substrates via paints is widely used in many sectors including the aerospace industry. The efficiency of the process depends on the durability of the paints and on the properties of the interface between the organic layer and the surface metal oxides; thus, the pre-treatment of the aluminium alloy prior painting is a very important step to long term -performance for this technology. However, most of the pre-treatments used now on the aluminium present environmental drawbacks as they are based on solvents and chromates. An alternative efficient and ecologically cleaner method is the plasma technology. In the present work, the aluminium substrates (Al-clad 2024) were cleaned by RF (13.56 MHz) plasma, from a mixture of oxygen and argon gases. It is observed that the carbon contamination is completely removed using Ar plasma. Thin SiO@sub x@ films have been deposited by plasma a mixture of hexamethyldisiloxane (HMDSO) and oxygen (20 W, 5 min). In the absence of oxygen, a thick (> 10 nm) and superhydrophobic (@theta@ @>=@ 100°) film characteristic of PDMS properties is formed; polysiloxane-like thin (< 10 nm) films (SiO@sub x@) are obtained with the introduction of oxygen (20, 50 and 80%). Both XPS and contact angle measurements confirmed both the composition and the structure of these films. More importantly, contact angle measurements using different liquids and interpreted with the van Oss Good Chaudhury theory, allowed to determine the surface free energy of the deposited films: the calculated surface tensions (@gamma@ @subs@, @gamma@ @subs@ @superd@, @gamma@@subs@ @super+@ and @gamma@@subs@ @super-@) of the film formed from HMDSO/O@sub 2@: 50/50 are in excellent agreement with those of reference silicium oxide substrates. @FootnoteText@ This work is supported by Walloon Region (RW n° 021/5208) in the framework of a collective reasearch project "ECOPO" in collaboration with Université de Mons-Hainaut and Coating Research Institute.

4:40pm **PS2-MoA9 Transparent Hybrid Inorganic/Organic Barrier Coatings for Plastic OLED Substrates*, T.W. Kim,*** GE Global Research Center*; M. Schaepkens,* GE Advanced Materials*; M. Yan, A.G. Erlat, M. Pellow, P.A. McConnelee, T.P. Feist, A.R. Duggal,* GE Global Research Center

The use of plastic film substrates enables fabrication of new applications in the area of flexible opto-electronics, such as flexible display and lighting, using low cost roll-to-roll fabrication technologies. One major limitation of bare plastic film substrates in these applications is the rapid oxygen and moisture diffusion through the substrates and subsequent moisture and oxygen induced degradation of the opto-electronic devices. Recently GE has developed a novel coating technology to reduce the moisture permeation rate through the plastic film substrate below 5x10@super-6@g/m@super2@/day using plasma enhanced chemical vapor deposition. Unlike other ultra-high barrier(UHB) coatings comprised of inorganic and organic multilayer, GE's UHB coating comprises a single layer of hybrid inorganic and organic materials. In this single layer, the composition is periodically modulated between silicon oxynitride and silicon oxycarbide. In addition, the transition from one material to the other is continuous, which results in a graded composition structure, so that there is no distinct interface between them. In contrast, other multilayer UHB coatings, where inorganic and organic materials are bound by relatively week van der Waals force, have sharp interface, which sometimes results in delamination of layers especially during the thermal cycle. Hardness and modulus of silicon oxynitride and silicon oxycarbide are tailored such that they are similar to those of typical glasses and thermo plastics, respectively. Modeling studies suggest that the polymer-like silicon oxycarbide enriched zone decouples the pinhole defects in the silicon oxynitride enriched zone compelling tortuous paths for moisture diffusion, and thus reduces the moisture permeation rate by seven orders of magnitude as compared to that of uncoated plastic substrates. GE's UHB coating also has superior visible light transmittance and color neutrality suitable for the use of display and lighting substrates.

5:00pm **PS2-MoA10 Mass Spectrometric Determination of the Mechanism of the Chemically-Enhanced Reaction of Hydrogen Plasmas and Propellant Surfaces.*, R. Blumenthal,*** *R. Valliere,* Auburn University

The erosion rate of sprayed-on films of the propellants RDX and HMX under hydrogen plasma exposure are more than one-hundred times the erosion rate in similar argon plasmas. Varying the plasma components impingent on the propellant surface (i.e. ions, radicals, electrons and light) by changing the sample bias and shielding the propellant surface reveals a number of strong synergistic interactions between the individual plasma components in the erosion of the film. Early supersonic pulse, plasma sampling, mass spectrometric studies have indicated that the erosion rate has both a fast and a slow component, but interferences in the mass spectrum have prevented the unambiguous identification of the products, and hence, the chemical mechanism. In this work, the volatile products collected during the erosion of isotopically labeled RDX and HMX will be presented along with a chemical/physical mechanism for the reaction.

Advanced Surface Engineering
Room 303D - Session SE-MoA

Structure Control of Hard Coatings in Sputtering Processes

Moderator: A.A. Voevodin, Air Force Research Laboratory

2:00pm **SE-MoA1 Control of Nanostructure Evolution in Metastable Transition Metal Nitride Layers using High-Flux, Low-Energy Ion Irradiation during Growth*, I. Petrov,*** University of Illinois **INVITED**

We use high-flux, low-energy ion irradiation during low-temperature growth to control the kinetic pathways of phase separation in metastable transition-metal nitride layers in order to produce novel nanostructures composed of self-organized nanolamellae in δ-TaN@sub x@ or nanocolumns in Ti@sub 1-x@Ce@sub x@N. Coherent δ-TaN(111)/γ-Ta@sub 2@N(0002) nanolamellae form spontaneously in reactively-sputter-deposited TaN@sub x@ layers when using ion energy E@sub i@ ~ 50 - 65 eV with an ion-to-metal flux ratio J@sub i@/J@sub Me@ ~ 11; at lower E@sub i@ the films are phase-pure metastable δ-TaN @sub x@. The nanolayers are coherent platelets of alternating metastable cubic δ -TaN@sub x@ and thermodynamically-stable hexagonal γ-Ta@sub 2@N phases which are lattice-matched along their hexagonal closed-packed δ-TaN(111) and γ-Ta@sub 2@N(0002) planes. The formation of γ-Ta@sub 2@N nanolamellae is attributed to ion-irradiation-induced ordering of N vacancies within the (111) N planes of δ-TaN that causes hexagonal stacking of the closed-packed Ta planes. The nanolamellar TaN layers exhibit superhardness values (H = 40-45 GPa). During reactive sputter-deposition of metastable Ti@sub 1-x@Ce@sub x@N alloys, we observe nanophase films with x>0.1. Under conditions of low ion-irradiation, i.e. grounded or floating substrates, the nanostructure consists of equiaxed grains which forms due to continuous renucleation induced by CeN segregation. This is analogous to the nanostructure to the one observed in crystalline/amorphous nanocomposites, e.g. TiN/Si@sub 3@N@sub 4@. In contradistinction, a novel nanocolumnar structure forms when the alloys are grown under intense ion-irradiation with J@sub i@/J@sub Me@ ~ 15 and Ei = 45 eV. The intense ion mixing in the near surface area allows sufficient adatom mobility to form local TiN- and CeN-rich areas that propagate along the growth direction.

2:40pm **SE-MoA3 Investigation of the Solubility in (M@sub x@M'@sub 2-x@)AlC (M and M' = Ti, V, Cr) as well as the Cr-Al-C System*, J.M. Schneider*,** *D. Music, Z. Sun, R. Mertens,* RWTH Aachen, Germany*; R. Ahuja,* Uppsala University, Sweden

We have performed theoretical studies of the solubility within (M@sub x@M'@sub 2-x@)AlC, where M and M' = Ti, V, Cr by means of ab initio total energy calculations. The theoretical values of equilibrium volume and the optimized c/a ratios are in good agreement with those of experiments (within ~ ± 4% and ~ ± 1.3%, respectively). Furthermore, we show that if x is increased from 0 to 2 the bulk modulus can be increased by as much as 36%. Based on the total density of states analysis as well as the energy of formation, we suggest that the investigated systems show solubility except for the (Cr,Ti)@sub 2@AlC system. In addition to these data we have studied the effect of the chemical composition on the structure in the system Cr-Al-C by combinatorial thin film synthesis. By changing the Cr/C ratio from 1.72 to 3.48 and the Cr/Al ratio from 1.42 to 4.18 the formation of Cr@sub 2@AlC, Cr@sub 2@Al and Cr@sub 23@C@sub 6@ phases was observed. Furthermore, based on X-ray diffraction a single phase Cr@sub 2@AlC composition region is identified (Cr/C ratio between 1.72 and 1.925, Cr/Al ratio between 1.42 and 2.03) in the Cr-Al-C phase diagram. Throughout the studied composition range the lattice parameters of Cr@sub 2@AlC were independent of the chemical composition : a = 2.865 Å ± 0.2%, c = 12.80 Å ± 0.6%. Furthermore, we find that a deviation from the stoichiometric composition of up to 6.3 at % for Al still results the formation of a Cr@sub 2@AlC single phase field. Possible pathways to accommodate the observed deviation from stoichiometry are discussed.

3:00pm **SE-MoA4 Growth and Characterization of New Epitaxial MAX-Phase Thin Films from the Ti@sub n+1@(Si, Ge)C@sub n@ Systems by Magnetron Sputtering**, ***H. Högberg***, *J. Emmerlich,* Linköping University, Sweden*; J.-P. Palmquist,* Kanthal AB, Sweden*; P. Eklund,* Linköping University, Sweden*; O. Wilhelmssson,* Uppsala University, Sweden*; L. Hultman,* Linköping University, Sweden*; U. Jansson,* Uppsala University, Sweden

This is a presentation of the state-of-the-art for the materials research on M@sub n+1@AX@sub n@ (n=1 to 3) phase thin films. The MAX-phases are a family of ductile inherently nanolaminated ternary nitrides and carbides with a high potential for industrial applications due to their unique combination of metallic and ceramic properties, as recently reported for the archetype Ti3SiC2. These properties stem from a highly anisotropic hexagonal crystal structure, where early transition metal (M) atoms and C or N (X) atoms form edge-sharing octrahedral MX blocks that are interleaved by layers of group 13-15 elements (A). Using DC magnetron sputtering with elemental sources we deposited epitaxial MAX-phase films from the Ti-Si-C and Ti-Ge-C systems on Al2O3(0001) or MgO(111) substrates at temperatures of 900 oC or 1000 oC, which is 500 oC lower than for conventional bulk processes. Besides demonstrating single-crystal growth of the known phases Ti3SiC2, Ti3GeC2, and Ti2GeC we have discovered two phases Ti4SiC3 and Ti4GeC3 as well as four intergrown structures of stoichiometries Ti5A2C3 and Ti7A2C5. The general trend from synthesis and characterization is that both MAX-phase systems show similarities with respect to phase distribution, mechanical, and electrical properties, reflecting the close chemical relationship between Si and Ge. However, XRD shows that the Ti-Ge-C MAX-phases are restricted to a more narrow deposition window and require slightly higher temperatures due to a more limited diffusivity of the larger Ge atoms. From the nanoindentation analysis we see the characteristic large plastic deformation with extensive pile up for both systems, but measure a slightly lower Youngs modulus of 300 GPa for the Ti-Ge-C films compared to the 320 GPa obtained from Ti3SiC2 films. The four-point probe measurements show a lower conductivity for the Ti3GeC2 films compared to their Si-counterparts with resistivity values of 50 and 25 @micro@@ohm@cm, respectively.

3:20pm **SE-MoA5 Epitaxial Growth of B1-NaCl-Structure HfN@sub x@ Layers on MgO(001) by Ultrahigh Vacuum Magnetron Sputter Deposition**, ***H.-S. Seo***, *T.-Y. Lee, J.G. Wen,* University of Illinois*; D. Gall,* Rensselaer Polytechnic Institute*; I. Petrov, J.E. Greene,* University of Illinois

Group IVB metal nitrides are used in hard coating, wear-resistant, and diffusion barrier applications due to their excellent mechanical, electrical, and electrochemical properties. In the Hf-N system, unlike Ti-N where TiN is the terminal phase, several conflicting claims concerning the existence of N-rich phases have appeared in the literature. Here, we report the results of a systematic investigation of the properties of epitaxial HfN@sub x@ layers grown at 650°C on MgO(001) by ultrahigh vacuum reactive magnetron sputter deposition in mixed N@sub 2@/Ar discharges. X-ray diffraction and transmission electron microscopy analyses show that HfN@sub x@ with 0.8 @<=@ x @<=@ 1.38 grows epitaxially with a cube-on-cube orientational relationship to the substrate. HfN@sub x@ layers with x @<=@ 1.2 are single crystalline while films with x @>=@ 1.24 consist of a mixture of NaCl-structure HfN@sub x@(001) and a N-rich phase with large interplanar spacing (d = 2.7-3.0 Å). The relaxed bulk lattice parameter of HfN@sub x@(001) decreases only slightly with N/Hf ratio from 4.543 Å with x = 0.8 to 4.504 Å with x = 1.38. The room-temperature resistivity @rho@ of HfN@sub x@ varies from 14.2 µ@ohm@-cm for x = 1.0 to 2710 µ@ohm@-cm for x = 1.5, while the hardness H and elastic modulus E values of HfN@sub x@(001) with 0.8 @<=@ x @<=@ 1.5 are 28±4 GPa and 400±60 GPa, respectively. HfN@sub x@(001) layers with 0.8 @<=@ x @<=@ 1.32 are metallic with positive temperature coefficients of resistivity (TCR) between 10 and 300 K and temperature-independent carrier concentrations. They are also superconducting with the highest critical temperature, 9.18 K, obtained for layers with x = 1.0. At higher N/Hf ratios (x @>=@ 1.38), the layers exhibit significant changes in their electronic structure leading to a dramatic increase in @rho@ with a negative TCR, no superconducting transition above 2 K, and a decrease in H and E.

3:40pm **SE-MoA6 Surface Morphological Evolution of Epitaxial CrN(001) Layers**, *J.R. Lynch, J. D'Arcy-Gall, S.V. Kesapragada,* ***D. Gall,*** Rensselaer Polytechnic Institute

CrN layers, 7 to 300 nm thick, were grown on MgO(001) at 600-800 @degree@C by ultra-high-vacuum magnetron sputter deposition in pure N@sub 2@ discharges at 20 mTorr. Microstructural and surface morphological evolution were found to depend strongly on the growth temperature T@sub s@. Layers grown at 600 @degree@C nucleate as single crystals with a cube-on-cube epitaxial relationship with the substrate. However, above a critical thickness of ~50 nm, misoriented CrN grains nucleate and develop into cone-shaped grains that protrude out of the epitaxial matrix to form triangular faceted surface mounds. These mounds lead to a dramatic increase in the root-mean-square surface roughness, from 3 to 19 nm, for a 300-nm-thick layer. CrN grown at T@sub s@ = 700 and 800 @degree@C are complete single crystals. Their surfaces exhibit dendritic mounds with fingers extending along orthogonal directions. In addition, the T@sub s@ = 700 @degree@C layer also shows square shaped "super"-mounds which protrude out of the underlying matrix and are attributed to a growth instability related to atomic shadowing effects which were purposely enhanced by non-normal deposition. For all layers, the surface roughness follows a power law with t. The exponent @beta@ is 1@+-@0.2 for the matrix-part of the surfaces, that is, the surfaces excluding the triangular and square shaped mounds for the T@sub s@ = 600 and 700 @degree@C layers, respectively. In contrast, @beta@ increases to 1.8@+-@0.3 when including the protruding grains. The two distinct @beta@-values are related to two roughening mechanisms: kinetic roughening, which is associated with an adatom motion towards ascending step edges due to a kinetic barrier for diffusion over descending steps, and atomic shadowing roughening, which is due to an increased local growth rate of surface protrusions caused by a higher capture rate of the incoming deposition flux.

4:00pm **SE-MoA7 Stress Reduction in Sputter Deposited Tungsten Films Using Nanostructured Compliant Layers by High Working-Gas Pressures**, ***T. Karabacak***, *J.J. Senkevich, G.-C. Wang, T.-M. Lu,* Rensselaer Polytechnic Institute

We present a new strategy of stress reduction in sputter deposited films by a nano-compliant layer at the substrate using physically self-assembled nanostructures obtained at high working-gas pressures prior to the deposition of a continuous film. This technique is all in-situ, and the nanostructures are made of the same material as the deposited thin film and requires no lithography process. This nanostructured layer has a lower material density and can act as a compliant layer to reduce the stress of the subsequently deposited continuous film grown under low gas pressure. By using this approach we were able to reduce stress values significantly in sputter deposited tungsten films and the strategy of alternating high and low Ar gas pressures leads to the growth of much thicker films without delamination.

4:20pm **SE-MoA8 High Powered Pulsed Magnetron Sputtering of Metallic Films in Ar, Ne, and He Plasmas**, *S.L. Rohde, J. Li,* ***D.M. Mihut,*** University of Nebraska-Lincoln

High Powered Pulsed Magnetron Sputtering (alternatively, HIPIMS) can yield peak plasma densities >10@super 13@ cm@super -3@, three orders of magnitude higher than conventional sputtering, and also results in a higher fraction of ionized sputtered material. For sputtering of Ti almost 100% ionization has been observed, while for Cu around 70% of the metal was ionized, as compared with 5 to 10% for conventional magnetron sputtering. In the present study, the ionization efficiency of HPPMS has been investigated as a function of working gas using Ar, Ne, and He to sputter a variety of metallic targets (Cr, Al, Ti, and Cu). Successful deposition was achieved using all three working gases, and it was determined that the percentage of ionized metal reaching the substrate surface in each case varies with gas pressure, pulse energy, target metal, and gas species. Even using He as the working gas, it was possible to generate a highly ionized Al-flux - a very unexpected result. Additionally, there are preliminary indications that this highly ionized flux may be utilized in interface engineering during etch and pre-deposition stages.

Selected films were studied both in-situ and ex-situ using spectroscopic ellipsometry (SE) to determine their optical properties and provide correlation between the optical properties and chemical/structural changes in the films, and thus providing a valuable resource for future work. In addition, some of these films were characterized post-deposition using X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), atomic force microscopy (AFM), and nanoindentation. XPS, AES, and SE were used in tandem to reveal the crystal structure of the films observed under specific growth conditions.

4:40pm **SE-MoA9 The Dominance of Oxygen in Two-Gas Reactive Sputtering of Oxynitride Films*, W.D. Sproul,* *D.C. Carter, D.J. Christie,* Advanced Energy Industries, Inc.

Reactive sputtering with two reactive gases and one target material presents special problems. Both reactive gases affect the state of the target surface and the plasma conditions, which means that both affect common feedback control signals such as the cathode voltage and optical emission signals. Modeling has shown that the way to control the two-gas reactive sputtering process is to produce individual control signals for each gas and to control the partial pressure of each reactive gas. Experiments have confirmed the model. When oxygen and nitrogen are the two reactive gases, oxygen usually dominates the reaction. A small change in the amount of oxygen results in large changes in the properties of the films, whereas it usually takes a large change in the nitrogen partial pressure to change the film properties. These results were found during two-gas reactive sputtering of the oxynitrides of aluminum, silicon, and titanium where a differentially pumped mass spectrometer was used to produce individual partial pressure feedback signals for the oxygen and nitrogen. For these three oxynitride systems, oxygen strongly dominated the reaction. Very slight changes in the oxygen to nitrogen partial pressure ratios result in large changes in rate and optical properties for these oxynitrides. The dominance of oxygen is particularly acute when flow control is used for the oxygen and the nitrogen is in partial pressure control. In this situation, it is possible for the oxygen to trap the target in a poisoned state that cannot be reversed until both gases are removed. To avoid this problem, partial pressure control should be used to control both reactive gases. Experimental results showing the dominance of oxygen over nitrogen for the two-gas reactive sputtering of AlOxNy, SiOxNy, and TiOxNy will be shown and discussed.

5:00pm **SE-MoA10 Ion Assisted Deposition of Zirconium Nitride using Balanced and Unbalanced Magnetron Sputtering*, S. Guruvenket,*** Indian Institute of Science, India, India

Zirconium nitride thin films were deposited on Si (111) substrates by balanced and unbalanced magnetron sputtering. The change in the preferred orientation of the deposited films was studied as a function of substrate bias voltage. ZrN films deposited by magnetron sputtering with out any bias voltage showed a preferred orientation of (111) where as, those deposited at higher bias voltages (above â?"60Volt) showed (200) as the preferred orientation. ZrN films deposited by unbalanced magnetron also showed a similar kind of transformation in the preferred orientation but the bias voltage required in this case was about -40V. Better quality films have been obtained with a resistivity value of 50 @micro ohm cm 1@ in unbalanced magnetron sputtering, where as, a resistivity of 63@micro ohm cm 2@ was obtained in case of magnetron sputtered ZrN thin films. The change in the surface roughness as the function of the bias voltage was also studied. @FootnoteText@ 1. @micro ohm cm 1@ 2. @micro ohm cm 2@.

Surface Science

Room 210B - Session SS1-MoA

Simulation and Theory of Adsorption

Moderator: S.B. Sinnott, University of Florida

2:00pm **SS1-MoA1 Theoretical Insights into Chemistry and Catalysis at the Aqueous Metal Interface*, M. Neurock,*** University of Virginia **INVITED**

The metal-solution interface is important in controlling a number of relevant processes including catalysis, electrocatalysis, and corrosion chemistry. Relatively little, however, is known about the structure and dynamics of the metal solution interface and its impact on elementary physicochemical surface processes, including adsorption, diffusion, and reaction. Density functional theory and ab initio molecular dynamic methods have been used to analyze the effects of aqueous media on the mechanism and the kinetics of different surface processes. The presence of protic solutions on well-defined metal substrates leads to a wealth of interesting surface behavior. Hydrogen bonding can modify the structure of adsorbed intermediates, alter the strength of the adsorbate surface-bond, stabilize charged intermediates, enhance surface kinetics and even provide new mechanistic pathways in which the solution directly participates. We describe the direct, as well as the indirect, effects of solution on different surface processes including the heterolytic dissolution of organic and inorganic intermediates, molecular and dissociative adsorption and desorption of organic intermediates over well-defined metal surfaces, surface reactivity, and diffusion. There are many cases where the solution can directly participate in these mechanisms by directly participating in proton transfer processes. These effects can be quite different in electrochemical systems since the chemical potential can have an important influence on the structure and reactivity at the metal solution interface. We examine here the energetics and pathways for methanol oxidation well-defined Pt(111) substrates over a range of different applied potentials for application to the direct methanol fuel cell.

2:40pm **SS1-MoA3 Atomistic Modeling of CO Oxidation on Pd(100): Ordering of the Reactant Adlayer, Bistability of Steady States, and TPR*, D.-J. Liu,*** *J.W. Evans,* Iowa State University

We develop a realistic atomistic lattice-gas model for CO-oxidation on Pd(100) under UHV conditions which describes equilibrium c(2@sq@2 x @sq@2)R45° ordering of CO(ads) on bridge sites, and both non-equilibrium c(2 x 2) and equilibrium p(2 x 2) ordering of O(ads) on four-fold hollow sites. The latter requires suitable treatment of the dissociative adsorption kinetics of O@sub 2@(gas) via an 8-site rule (reflecting strong repulsions between neighboring O) together with transient mobility. CO-CO and O-O adspecies interactions are tuned to match experimental LEED, TPD, and heat of adsorption data for the separate adspecies. Description of the interaction and reaction between CO(ads) and O(ads) is guided by DFT results and by comparison with TPR data. With this model, we map out the bifurcation diagram for the reactive steady states identifying the bistability regime and critical (cusp) point. We also relate various features of the experimental TPR spectra to details of the adspecies interactions in this system. We also discuss extension of the model to the regime of higher pressures, where oxide formation produces a clear signature in the TPD spectra for oxygen, and impacts the reaction kinetics.

3:00pm **SS1-MoA4 CO Coupling Reaction on UO@sub2@(111)Single Crystal Surface: An Experimental and Theoretical Study*,*** *H. Idriss,* ***S.D. Senanayake,*** *A.S.L. Soon,* The University of Auckland, New Zealand

The unique electronic properties of UO@sub2@ makes it an ideal prototype material for investigation of new chemical pathways. Carbon monoxide molecules were found to selectively couple to C2 compounds over O-defected surfaces of UO@sub2@(111) single crystal. The most plausible reaction can be described by: 4CO + H@sub2@ -> C@sub2@H@sub2@ + 2CO@sub2@. This unique reaction is studied using temperature programmed desorption (TPD), X-ray Photoelectron Spectroscopy (XPS) and valence band, targeting surface intermediates and oxidation states of uranium and oxygen ions. Evidence of CO dissociation upon adsorption is seen by the disappearance of XPS lines due to U metal, the increase of those related to U@super4+@ and the formation of surface carbides. Preliminary steady state catalytic experiments on polycrystalline H@sub2@-reduced UO@sub2@ have further confirmed the selective pathway to acetylene and ethylene. Relativistic density functional theory (DFT) calculations have been performed using the Amsterdam Density Functional Theory for molecules and with BAND code for embedded clusters and periodic slab studies. Binding energies and conformations of CO adsorption on the surface are probed to offer a deeper understanding of surface energetics. The structures of interests were fully optimised with the inclusion of scalar relativistic effects, which were treated with the Zeroth-Order Regular Approximation (ZORA) formalism.

3:20pm **SS1-MoA5 Towards an Understanding of the Silver Catalysed Ethylene Epoxidation Process*, A. Michaelides,*** University of Cambridge, United Kingdom*; K. Reuter, M. Scheffler,* Fritz-Haber-Institut der Max-Planck Gesellschaft, Germany

A number of recent studies indicate that, under moderate pressures of oxygen, some transition metal catalysts are covered in thin oxide overlayers. For oxidation catalysis, it has been suggested that such "surface-oxide" layers are catalytically active, and that this role is not performed by the pure metal surfaces as was traditionally assumed. This contemporary picture can be traced back to Ag catalysis, where it has been believed for 30 years that exposure of oxygen to Ag{111} leads to the formation of an ultra-thin surface-oxide. Extensive experimental and theoretical work has been carried out for oxygen on Ag, motivated mainly by the desire to understand silver's unique ability as a partial oxidation catalyst for ethylene [see, for eg., refs. 1-4]. However, density functional theory results, presented here, augmented with thermodynamic calculations, indicate that previous conclusions are significantly incomplete and that the structure of this original surface-oxide must be reconsidered. Indeed novel oxide overlayers are identified, and, predicted to be stable under the oxygen pressures at which the industrial ethylene epoxidation reaction is carried out. Moreover, we find that under these conditions finite variations in the stoichiometry of the surface oxides can occur with practically no change in free energy. It is suggested that this is one of the essential hallmarks of an effective red-ox catalyst. The first phase diagrams of Ag in contact with gaseous environments of both oxygen and ethylene are also be presented, as are reaction mechanisms for the formation of ethylene-epoxide. @FootnoteText@ @footnote 1@C.T. Campbell, J. Catal. 94, 436 (1985). @footnote 2@C.I. Carlisle, M.-L. Bocquet, J. Cerda, D.A. King, P. Sautet, Phys. Rev. Lett. 84, 3899 (2000). @footnote 3@A. Michaelides, M.-L. Bocquet, P. Sautet, A. Alavi, D.A. King. Chem. Phys. Lett. 367, 344 (2002). @footnote 4@W.X. Li, C. Stampfl, M. Scheffler, Phys. Rev. B 68, 165412 (2003).

3:40pm **SS1-MoA6 Determination of Adsorption Site for Isocyanides and Aminocarbynes on Pt(111) from Theoretical and Experimental Vibrational Spectra***, **E. Herceg**, B. Chatterjee, M. Trenary,* University of Illinois at Chicago

Density funcional theory (DFT) calculations have been used to study the bonding, geometry, and influence of basis set size on the vibrational properties of methyl-isocyanide (CH@sub 3@NC) and aminocarbyne species (CNH@sub 2@ and CNHCH@sub 3@) bonded to different Pt clusters. Calculated spectra were compared with the RAIRS data obtained for the corresponding species adsorbed on the Pt(111) surface. We used Pt, Pt@sub 7@H@sub 6@, Pt@sub 2@, Pt@sub 9@H@sub 14@, and Pt@sub 4@ clusters in order to provide models for adsorption at on-top, two-fold bridge, and three-fold hollow sites. Comparison between experimental and calculated spectra showed that CH@sub 3@NC is bonded to the surface at on-top site for low coverages and at both on-top and bridge sites for high coverages. For aminocarbynes bonded to Pt@sub 2@ and Pt@sub 9@H@sub 14@ (models of the twofold bridge site) calculations successfully reproduce experimental spectra. No significant improvement was achieved by using the Pt@sub 9@H@sub 14@ cluster compared with the Pt@sub 2@ model. On the other hand better agreement between experimental and simulated spectra of CH@sub 3@NC and CNH@sub 2@ can be achieved by increasing the size of the basis sets used for both the adsorbate and Pt cluster atoms.

4:00pm **SS1-MoA7 Ab Initio Molecular Dynamics Study of Methanol Adsorption and Reaction on Copper Clusters***, **W.-D. Hsu**, S.B. Sinnott,* University of Florida

The reaction of methanol molecules with size-selected Cu@sub n@ clusters, n=2-9, is investigated by first-principles molecular dynamics simulations. The simulations use density functional theory within the generalized gradient approximation and ultrasoft pseudopotentials. The molecules are deposited on the Cu clusters with an incident energy of 0.5 eV/molecule. The structure, dynamics, and reaction energy are studied as a function of the cluster size. Experiments by Kondow and co-workers@footnote 1@ find that the dominant reactions are methanol chemisorption, demethanation, and carbide formation, which are very different from the interaction of methanol with bare copper surfaces, where physisorption is the dominant outcome. The simulations detail the atomic scale mechanisms that are responsible for these differing behaviors. For example, they show that the adsorption energy of methanol to Cu@sub 7@ is about 0.5 eV, which is larger than the energy of adsorption of methanol on the Cu(111) surface@footnote 2@@super ,@@footnote 3@ by about 0.25 eV. The simulations also illustrate the differences in the interaction of methanol with copper clusters of various sizes. This work is supported by the National Science Foundation (CHE-0200838). @FootnoteText@ @footnote 1@M. Ichihashi, T. Hanmura, R. T. Yadav, and T. Kondow, J. Phys. Chem. A 104 (2000) 11885@footnote 2@J. R. B. Gomes, and J. A. N. F. Gomes, Surf. Sci. 471 (2001) 59@footnote 3@J. Greeley, and M. Marvrikakis, J. Cataly. 208 (2002) 291.

4:40pm **SS1-MoA9 Furan Decomposition Mechanism on Vicinal Pd(111) Studied by STM and DFT@footnote 1@***, **A. Loui**, C.Y. Fong, S. Chiang,* University of California, Davis

We have used scanning tunneling microscopy to investigate the behavior of furan (C@sub 4@H@sub 4@O) adsorbed intactly on stepped Pd(111) at 199 and 225 K, as well as aspects of its decomposition after heating to a maximum temperature of 415 K. Studies conducted on two substrates with relatively narrow and wide terraces reveal strikingly different behaviors. Furan is shown to preferentially adsorb at step edge sites on both surfaces, while evidence of molecular diffusion is seen only on the narrower vicinal planes. After heating to 288 K, 300 K, and 415 K, evidence of reaction can be observed in occupied-states STM images. Our observations support a furan decomposition mechanism wherein the heterocycle preferentially adsorbs and reacts at upper step edge sites. Although our data do not provide a complete picture of the surface reaction, the proposed model is consistent with previous studies of surface adsorption, diffusion, and reaction on vicinal, low-Miller-index transition metal surfaces. Ab initio calculations based on Hohenberg-Kohn density functional theory (DFT) have been performed for several high-symmetry adsorption modes of furan on flat Pd(111). These results, optimized with respect to planewave basis size and k-point sampling of the Brillouin zone, show that a two-fold chemisorption site is energetically preferred over the three-fold hollow and on-top sites. @FootnoteText@ @footnote 1@ Funded by NSF CHE-0111671.

Surface Science
Room 210C - Session SS2-MoA
Assembled Monolayers

Moderator: M.R. Linford, Brigham Young University

2:00pm **SS2-MoA1 Surface Liquid Behavior of Organic Molecules in Nanoscale Direct Deposition Processes***, **N. Cho**, S. Hong,* Seoul National University, South Korea

Nanoscale direct deposition processes such as dip-pen lithography (DPN) have been extensively utilized to pattern organic molecules on solid surfaces. However, complicated 2-dimensional nanoscale diffusion phenomenon in the DPN process has not been clearly understood yet. We propose the surface liquid-based diffusion model that can fully explain complex humidity and temperature dependence of dip-pen lithography. In addition, the study of the long term dependence of DPN deposition rate and phase-separation in the mixed molecular system revealed strong intermolecular interactions during the DPN diffusion process, which also confirms our surface liquid model.

2:20pm **SS2-MoA2 The First Demonstration of the Gas Phase Modification of Scribed Silicon***, **M.V. Lee**,* Brigham Young University*; S.M. Casey,* University of Nevada, Reno*; M.R. Linford,* Brigham Young University

Chemomechanical Surface Functionalization (CMSF) is a simple and versatile method for patterning and functionalizing silicon surfaces. Using this method very small (ca. 30 nm) features have been scribed on silicon using an AFM, as well as much larger features (many microns) using a diamond tip. To date, CMSF has been demonstrated with a variety of neat liquids, including different alkenes, alkynes, alkyl halides, alcohols, aldehydes, and epoxides. However, in spite of the power of this approach for the direct modification of silicon at any desired point on its surface, a drawback of this method is that the unreacted liquid must be removed from the surface by washing following CMSF. Washing creates an opportunity for unwanted surface reactions and/or surface contamination. A CMSF method that would eliminate the surface cleaning step would be an important advance for this technique. Here we show that that two gas phase reagents (ethylene and acetylene) react with scribed silicon. It is noteworthy that this process takes place in an open laboratory using a simple laboratory apparatus that directs a jet of these reactive gases onto the silicon surface during scribing. The resulting surfaces were characterized by X-ray photoelectron spectroscopy, wetting, time-of-flight secondary ion mass spectrometry, Auger electron spectroscopy, and temperature programmed desorption. @FootnoteText@ Niederhauser, T.L.; Lua, Y.-Y.; Jiang, G.; Davis, S.D.; Matheson, R.; Hess, D.A.; Mowat, I.A.; Linford, M.R. Arrays of Chemomechanically Patterned Patches of Homogeneous and Mixed Monolayers of 1-Alkenes and Alcohols on Single Silicon Surfaces. Angew. Chem. Int. Ed. 2002, 41(13), 2353-2356.

2:40pm **SS2-MoA3 Displacement Printing of Adamantanethiolate Self-Assembled Monolayers***, **A.A. Dameron**, R.K. Smith, J.R. Hampton, P.S. Weiss,* The Pennsylvania State University

We have fabricated 1-adamantanethiolate self assembled monolayers (SAMs) on Au{111} and characterized them with scanning tunneling microscopy (STM). The adamantanethiolate SAMs are highly ordered and have less prominent domain boundaries than alkanethiolate SAMs, but the adamantanethiolate molecules are easily displaced by other molecules both during and after SAM formation. Taking advantage of this displacement, we have used adamantanthiolate SAMs in conjunction with microcontact printing to pattern molecules that are difficult to microcontact print by normal methods. Using STM and lateral force microscopy (LFM) we have studied the molecular order of the printed features.

3:20pm **SS2-MoA5 Controlling Surface Architecture on the sub-100 nm Length Scale with Dip-Pen Nanolithography***, C.A. Mirkin, **K. Salaita**,* Northwestern University **INVITED**

Dip-Pen Nanolithography (DPN) is a scanning-probe technique that permits the chemical functionalization of surfaces with nanoscale precision. Based upon a conventional Atomic Force Microscope, DPN combines ambient operation and resolutions superior to those of e-beam lithography, and allows one to create combinatorial libraries of soft matter nanostructures that can be used in fundamental surface science studies, biological diagnostics, and organic nanoelectronics. This talk will describe the fundamental capabilities of DPN and its use to generate and study a wide variety of nanostructures using materials ranging from oligonucleotides to proteins to conjugated polymers. Moreover, recent efforts to transform DPN into a high throughput tool through the use of 1 million pen cantilever arrays will be presented.

4:00pm **SS2-MoA7 Competition as Design Concept in Self-Assembled Monolayers***, **P. Cyganik**, M. Buck,* St Andrews University, UK

Self-assembled monolayers (SAMs) of aromatic thiols adsorbed on Au(111) substrates were studied using scanning tunneling microscopy (STM). Our experiments show that a molecular design, which is not based on the usual concept of energy minimization but employs competing forces, opens an unexpected additional dimension in the control of structure and properties of thiol SAMs. Based on thiols which are characterized by a combination of a biphenyl unit and an alkane spacer (CH@sub 3@(C@sub 6@H@sub 4@)@sub 2@(CH@sub 2@)@sub n@SH, BPn, n = 2, 3, 4, 5, 6), the length of the spacer is chosen such that different factors which determine the energetics of a SAM structure (e.g. sulfur bonding geometry vs. intermolecular interactions) enter in a competing rather than a cooperative way. The SAMs prepared according to this concept show thermally induced irreversible transitions into new structures. This transition is paralleled by striking improvement in the structural perfection of the SAM and changes in the stability against exchange by other thiols.

4:20pm **SS2-MoA8 Tuning of Orientation and Chiral Recognition of a Single Chiral Molecule in Self-Assembly through Modulation of Anchoring Sites***, **B.I. Kim**,* Boise State University*; C.Z. Cai, S.S. Perry,* University of Houston

Rod-like aromatic systems with conducting @pi@-backbones are of interest as potential building blocks for electronic devices. Hydrogen bonding could be used as a conductive linkage of molecular wire on a surface. When we build up a self-assembly with rod-like molecules on a surface through hydrogen bonding, we can use chirality to control the configuration of the nanostructure. Recent studies show that chirality plays an important role in site-specific adsorption of molecules, formation of extended chiral domains, and enhancement of stability of clusters and chains. However, those observations have been limited to specific chiral adsorption configurations without addressing more tunable modification of them for a novel nano-engineering. Here we present scanning tunneling microscopy studies of a chiral molecule with two functionalized benzene rings, 4-trans-2-(pyrid-4-yl-vynyl) benzoic acid(PVBA), on surfaces. PVBA shows chiral separation on Ag(111) but not on Pd(111) while it shows orientational separation on Pd(111) but not on Ag(111). An angle dependent model calculation indicates that the orientation and chiral recognition could be tuned through modulation of double anchoring sites, applicable for flexible nano-wire and chiral separation on the surface.

4:40pm **SS2-MoA9 Resonance-Assisted Hydrogen Bonds Stabilize Guanine Quartet Networks on Solid Surfaces***, **R. Otero**, M. Schöck, L.M. Molina, E. Laegsgaard, I. Stensgaard, B. Hammer, F. Besenbacher,* University of Aarhus, Denmark

Hydrogen bonding between DNA bases is one of the main interactions that control the conformation and hence the biochemical function of nucleic acid molecules@footnote 1,2@. Apart from the Watson-Crick model for base pairing@footnote 1@, DNA bases can form other hydrogen-bonded complexes that lead to different DNA structures, like G-quadruplexes@footnote 3@ or i-motifs@footnote 4@. In spite of the increasing evidence for the existence and in vivo function of these DNA structures@footnote 5@, a convincing biophysical model for their stability is still missing. By combining high-resolution, variable-temperature Scanning Tunneling Microscopy (STM) and state-of-the-art Density Functional Theory (DFT), here we show that the DNA base guanine (G) deposited under ultra-clean conditions onto a suitably inert substrate such as Au(111) self-assembles into a hydrogen-bonded network of G-quartets, whose structure corresponds perfectly with the quartet structure of telomeric DNA@footnote 3@ determined by X-ray crystallography. The strong preference of G molecules to form quartets can be explained by a cooperative effect that strengthens the hydrogen bonds within the G-quartet network over the hydrogen bonds in isolated dimers. This result underlines the necessity of going beyond the picture of isolated hydrogen bonds in order to properly describe the interactions between biomolecules. @FootnoteText@ @footnote 1@ Watson, J. D. & Crick, F. H. C. A structure for deoxyribose nucleic acid. Nature 171, 737-738 (1953).@footnote 2@ Sinden, R. R. DNA Structure and Function (Academic Press, San Diego, 1994).@footnote 3@ Sundquist, W. I. & Klug, A. Telomeric DNA dimerizes by formation of guanine tetrads between hairpin loops. Nature 342, 825-829 (1989).@footnote 4@ Gehring, K., Leroy, J.-L. & Guéron, M. A tetrameric DNA structure with protonated cytosine-cytosine base pairs. Nature 363, 561-565 (1993).@footnote 5@ Kipling, D. The telomere (Oxford University Press, Oxford, 2002).

Thin Films
Room 303C - Session TF-MoA
Mechanical Properties of Thin Films

Moderator: B.L. French, College of William and Mary

2:00pm **TF-MoA1 Nano-Mechanical Properties of a "Solid Liquid"***, **J.E. Houston**,* Sandia National Laboratories

Understanding the unique properties of nano-phase materials requires analysis of the mechanical properties at the nano-scale. Since many such materials involve the inclusion of small particulates in a polymer matrix, it is important to be able to analyze the viscoelastic behavior of the matrix in the region adjacent to the particulates, the so called â?ointerphaseâ?□ region. Scanning probes have the potential to be very important for this type of analysis. However, such applications are made difficult because of the critical role played by contact mechanics in the process, and at the nano-scale this quantity is not directly observable. In this presentation, an example of such an analysis is outlined involving a classic viscoelastic material, which is often referred to as a â?osolid liquidâ?□ or â?odilatantâ?□ material, but is more commonly known under the popular name â?oSilly PuttyTMâ?□ (trademark: Binney and Smith). This material is unusual because it exhibits elastic behavior over short experimental times (high Deborah numbers) and viscous properties over long times (low Deborah numbers). The results are presented in terms of transient relaxation measurements, using both lyophilic and lyophobic tips, followed by a Fourier analysis to obtain the broad-range frequency response. These results are directly compared with more classical bulk rheological measurements. While these initial results are not done at the true nano-scale, the discussion will include an assessment of the potential, and contact-mechanics difficulties, involved in proceeding to that regime. Sandia is a multi-program laboratory operated by Sandia Corporation, a Lockheed Martin company, for the DOE under Contract DE-AC04-94AL85000.

2:20pm **TF-MoA2 Structure and Properties of Exothermic Metal Multilayers***, **D.P. Adams**, C. Tigges, M.A. Rodriguez, T. Buccheit,* Sandia National Laboratories

Multilayer thin films composed of reactive material pairs are currently of interest for brazing, joining and other applications. As shown extensively by Weihs et.al. several thin film material systems can be stimulated such that a rapid, self-propagating reaction occurs within a multilayer. These layers have great potential for joining, because they act as a localized, short-lived heat source. In this talk, we evaluate the properties and microstructure of two multilayer systems, Co/Al and Pt/Al, which have vastly different heats of formation. Each material system was deposited by magnetron sputtering to thicknesses in excess of 1 micron having different designs. Propagation velocities were measured by high-speed photography for both material systems, and speeds are shown to depend on bilayer thickness, premixed volume, heat of formation and substrate thermal properties. Critical thicknesses required for propagation (when attached to substrates) have been identified and are described through comparison with analytical models. Secondly, we discuss the microstructure and mechanical properties of reacted films. New (previously not reported) phases have been found after exhibiting a self-propagating exothermic reaction. For example, rhombohedral AlPt has been produced in reacted Al/Pt multilayers. We currently attribute this to the rapid quench rate following reaction to high combustion temperatures. The mechanical properties (hardness, toughness) of reacted films are also investigated, because these are critical to future applications. Attempts are made to relate these properties to reacted film microstructure.

2:40pm **TF-MoA3 A Nanometrics Feasibility Approach to Reliable Devices**, ***W.W. Gerberich***, *W.M. Mook, J.M. Jungk, M.J. Cordill,* University of Minnesota **INVITED**

Rapid advances in LIGA structures and other approaches to MEMS devices could be achieved by fast turn-around screening. This could be achieved on appropriate length-scale test samples fabricated by MBE (molecular beam epitaxy), CVD (chemical vapor deposition), ALD (atomic layer deposition), and electrochemically-produced small volumes. Using nanoindenters as either indenters or compression testers, we have already demonstrated that films, nanospheres, and thin-walled nanoboxes of Au, Ti and Si can exhibit three or four levels of length scale.@footnote 1@ These and further developments regarding possible computational and combinational approaches will be discussed. @FootnoteText@ @footnote 1@W.M. Mook, "Geometry and Surface State Effects on the Mechanical Response of Au Nanostructures," Zeiss Metalkunde (2004) in press.

3:20pm **TF-MoA5 Properties and Applications of Boron Carbide Thin Films**, ***Y. Chen***, *C.A. Freyman, Y.-W. Chung,* Northwestern University

Boron carbide thin films have been synthesized with pulsed dc magnetron sputtering using a boron carbide target in an ambient of pure argon. We examined the effect of substrate bias and pressure on the surface roughness and hardness of these films. Wear rates and coefficient of friction data were also obtained. As expected, an optimum substrate bias results in the atomic scale surface topography and highest nanoindentation hardness (about 40 GPa). Under normal ambient conditions, boron carbide films result in lower friction coefficient, most likely due to the formation of boric acid as a solid lubricant, reported earlier by Erdemir and coworkers. The high hardness, smooth topography and low friction even in moist environments suggest that boron carbide may be a better protective overcoat for disk drive systems.

3:40pm **TF-MoA6 Mechanical Stress in PVD Deposited Chromium Films**, ***G.C.A.M. Janssen,*** Delft University of Technology, The Netherlands, Netherlands; *J.-D. Kamminga, S.Y. Grachev,* Netherlands Institute for Metals Research, The Netherlands

Thin films on substrates are usually in a stressed state. Apart from the well understood thermal stress - stress occurring due to different thermal expansion coefficient of layer and substrate in combination with an elevated deposition temperature - intrinsic stress can occur resulting from the growth and/or microstructure of the film. In this presentation the mechanisms behind both tensile and compressive intrinsic stress are discussed. A set of chromium films was deposited at room temperature using PVD. These films have a microstructure in zone 2 of the Thornton model. The grain boundary density is high near the substrate-film interface and lower higher up in the film. In fact the grain boundary density as function of height in the film follows a power law. We have shown that tensile stress and grain boundary density co-develop with film thickness. This observation proves the generation of tensile stress at grain boundaries. We calculated the amount of grain boundary shrinkage responsible for the generation of tensile stress to be 0.013 nm. Films deposited at higher Ar pressure exhibit a different power law dependence on thickness. TEM revealed dense grain boundaries and small grains for the films deposited at low pressure and porous grain boundaries, separating larger feather like grains, for films deposited at higher pressures. Grains in those films have less interaction and generate less stress. Stresses in films deposited under a bias voltage were tensile for thin films and compressive for thick films. This is due to a combined effect of atomic peening, leading compressive stress and grain boundary shrinkage leading to tensile stress. It is shown that the dependence of the total stress on film thickness is described by a thickness dependent tensile term and a thickness independent compressive term.

4:00pm **TF-MoA7 Development of Zrb@sub 2@ and Hfb@sub 2@ Hard Coatings by CVD from Single Source Precursors**, ***S. Jayaraman***, *E.J. Klein, Y. Yang, L. Nittala, J.R. Abelson, D.Y. Kim, G.S. Girolami,* University of Illinois at Urbana-Champaign

The transition metal diborides ZrB@sub 2@ and HfB@sub 2@ are "metallic ceramic" materials with excellent properties, including high melting temperature (> 3000 °C), low electrical resistivity (9 µm@ohm@cm for ZrB@sub 2@), high thermal conductivity (23 Wm@super -1@K@super -1@ for ZrB@sub 2@), high hardness (20 and 29 GPa for ZrB@sub 2@ and HfB@sub 2@, respectively), and great corrosion resistance. This makes them attractive candidates for monolithic or nanocomposite based hard coatings. However, there have been relatively few attempts to deposit transition metal diboride coatings by chemical vapor deposition (CVD). Here, we investigate ZrB@sub 2@ and HfB@sub 2@ growth by CVD using the single-source precursors Zr[BH@sub 4@]@sub 4@ and Hf[BH@sub 4@]@sub 4@ over the substrate temperature range 200-1000 °C. At temperatures < 500 °C, we direct a flux of atomic hydrogen, generated by a remote plasma source, onto the growth surface in order to promote the removal of excess boron and improve stoichiometry. For deposition temperatures < 500 °C the films appear to be amorphous in X-ray diffraction; for higher temperatures crystalline peaks are detected. The crystalline films are strongly textured with either (0001) or (10@super-@10) planes normal to the growth direction and display characteristic microstructures. Initial experiments on trench coverage at low temperatures show that film growth is conformal. We will report the hardness of ZrB@sub 2@ and HfB@sub 2@ films determined by nanoindentation and the relationship between the hardness, crystallinity, and microstructure. We will also outline the prospects for the growth of nanocomposite hard coatings in this materials system.

4:20pm **TF-MoA8 Effects of Sulfur Addition to Magnetron Sputtered a-C:H Thin Films**, ***C.A. Freyman***, *Y.-W. Chung,* Northwestern University

Amorphous hydrogenated carbon films (a-C:H) have shown ultra low friction coefficients (µ<0.01) in dry nitrogen testing environments. The ultra low friction properties degrade with the addition of water vapor to the testing environment. In this work, we explore the effects of sulfur addition to magnetron sputtered a-C:H films on elastic modulus, hardness and tribological properties as a function of relative humidity in the testing environment. Film microstructure and chemical state of sulfur have been investigated with transmission electron microscopy and electron energy loss spectroscopy. Hydrophobicity of these films are obtained via contact angle measurements. These studies show that with appropriate control of the film-substrate interface, sulfur addition of a few atomic percent is sufficient to reduce the adverse effect of humidity on friction.

4:40pm **TF-MoA9 RF MEMS Beam Stiffness Measurement Using Nanoindentation**, ***J. Vella***, *S. Pacheco, P. Zurcher,* Freescale Semiconductor

With wireless communications being a major technology driver for semiconductors, on-chip integration of analog functions that are often based on passive components is crucial for reduced system form factor, higher performance, improved functionality, and reduced cost. MEMS-based resonators promise to deliver smaller and more easily integrated IF and RF filters and oscillators. The operating frequency of such filters and oscillators is defined by the mechanical resonant frequency and is given by @omega@@sub n@=@sr@(k/m), where @omega@@sub n@ is the natural resonant frequency, k is the beam stiffness and m is the beam mass. Thus, direct determination of the beam's stiffness is paramount for the design of MEMS-based resonators. The stiffness, k, can be determined for a fixed-fixed beam under a concentrated load at its center using the following equation: k=16Ew@sub r@(h/L@sub r@)@super 3@, where E is the Young's modulus of the beam material, w@sub r@, h, and L@sub r@ are the width, thickness, and length of the fixed-fixed beam, respectively. This study compares modeled beam stiffness predictions with nanonindentation measurements. A 20 µm radius diamond tip is used to deflect a resonator laminate beam composed of tantalum nitride and silicon oxynitride. Nanoindentation loads are used to induce elastic deflection of the resonator beam. The unloading portion of the nanoindentation load versus deflection curve directly yields the beam stiffness. This measurement technique was used to determine the stiffness of several resonator beam designs. Stiffnesses in the 900-5000 N/m range were measured and were within 10% of the calculated values using the above stiffness equation. In addition, derived stiffnesses from measured beam resonant frequencies (as per the resonant frequency equation above) further confirm the nanoindentation measurements.

5:00pm **TF-MoA10 Effect of Trimethylsilylation on the Film Stress of Nanoporous Silica Ultralow-k Film Stacks***, **F.M. Pan,*** National Chiao Tung University, Taiwan*; A.T. Cho,* National Nano Devices Laboratories, Taiwan*; J.Y. Chen, L. Chang,* National Chiao Tung University, Taiwan*; K.J. Chao,* National Tsing Hua Univerisity, Taiwan

In advanced dual damascene interconnect structures, ultralow-k dielectrics must be integrated with etch stop and barrier layers, and, therefore, interfacial properties of the film stacks are critical to process yield and reliability of interconnects. In this work, the film stress and effective dielectric property of self-assembled nanoporous silica overcoated by various dielectric thin layers were studied. The nanoporous silica was prepared by spin-coating the sol-gel precursor on the silicon wafer, followed by baking and calcination. Due to the film shrinkage during thermal treatments, the as-prepared nanoporous silica films have a tensile film stress. In order to improve the dielectric property, the nanoporous silica thin film was exposed to hexamethyldisilazane (HMDS) vapor for trimethylsilylation, and a dielectric constant lower than 1.95 could be obtained. The film stress became less tensile after the HMDS treatment. The decrease of the tensile stress can be ascribed to the spring-back effect resulting from the introduction of bulky trimethylsilyl groups in the nanoporous silica layer. Three different capping layer, Si@sub 3@N@sub 4@, SiO@sub 2@ and @alpha@-SiC:H films were separately deposited on the nanoporous film at 300@sup o@C. When directly deposited on the Si wafer, all the three capping materials show compressive stress. While the capping layers were deposited on the as-calcined nanoporous silica, the film stress of the SiO@sub 2@ and Si@sub 3@N@sub 4@ layers was so large that the capping layers cracked. On the other hand, when the capping layers were deposited on the HMDS treated nanoporous silica, the film stacks showed no mechanical failure and the effective dielectric constant could be lower than 2.2. This study suggests that trimethylsilylation of the nanoporous silica low-k dielectric can effectively improve the integrity of the three film stacks in terms of mechanical strength and dielectric property.

Applied Surface Science
Room Exhibit Hall B - Session AS-MoP
Poster Session

AS-MoP1 Producing Substrates for MALDI-MS by Chemomechanically Scribing Silicon and Glass., ***R. Blake***, *G. Jiang, C. Thulin, M.R. Linford,* Brigham Young University

Miniaturized matrix-assisted laser desorption/ionization mass spectrometry (MALDI-MS) sample supports have been developed on silicon and glass for improving analysis sensitivity and reproducibility of biomolecules. Clean silicon and glass were silanized with a fluorinated compound that produces extremely hydrophobic surfaces. After silanization 200 micron diameter hydrophilic anchors were chemomechanically scribed with a diamond tip onto silicon and glass in the presence of water. These hydrophilic areas pin aqueous solutions of matrix and peptide. As the water evaporates the matrix and peptide are pinned to the hydrophilic areas, concentrating and localizing the analyte to a small spot that is fully covered by the ionizing laser beam. Thus, both sensitivity and reproducibility of the analysis are simultaneously improved. MALDI-MS spectra of water soluble peptides, glufibrinopeptide B and angiotensin II, with 2,5-dihydroxy benzoic acid (DHB) as matrix on silicon or glass substrates showed the expected improvements both in sensitivity and reproducibility. Compared to previous reports, this method of making miniaturized MALDI-MS sample supports is rapid, cheap, and could be undertaken in a typical laboratory.

AS-MoP2 TOF-SIMS Investigation of Selected Excipients in Color Coated Placebo Tablets, ***X. Dong***, *C.A.J. Kemp,* Eli Lilly and Company

Time of Flight-Secondary Ion Mass Spectrometry (TOF-SIMS) was applied to investigate the surface and cross-section of placebo tablets. Eight excipients, including lactose, hydroxypropyl cellulose (HPC), and microcrystalline cellulose (MCC) were examined, as well as color coat mixture and polishing material used in placebo tablets. The investigation of raw materials shows that HPC can be distinguished from other excipients based on its unique peaks present in positive ion TOF-SIMS spectra. Most peaks observed in the spectra of MCC were also detected in the spectra of lactose, which makes it difficult to distinguish MCC from lactose. The comparison between the spectra obtained from tablet surface and cross-section shows that the chemical composition of tablet surface is different from that of bulk. Mg, which comes from a polishing material used on the outside of the tablet, dominates placebo surface spectra, while Na, which is one of constitutes of several excipients, dominates the cross-section spectra. In addition, peaks corresponding to HPC were much more abundant in the surface spectra than in the cross-section spectra, comparing to peaks corresponding to MCC/lactose. The preliminary results suggest that HPC might migrate more easily to sample surface than MCC and lactose during the tablet manufacturing process. The possibility of surface contamination is relatively low, since HPC related peaks were consistently found in surface spectra of all placebo tablets examined, as well as one house drug tablet analyzed in previous work.

AS-MoP3 Cluster Primary Ion Bombardment Facilitates ToF-SIMS Analysis of Biological/Tissue samples, ***V.S. Smentkowski***, General Electric Global Research Center; *A. Schnieders,* Ion-Tof USA, Inc.; *F. Kollmer,* Ion-Tof GmbH; *R. Kersting,* Tascon GmbH, Germany; *J.A. Ohlhausen, M.R. Keenan, P.G. Kotula,* Sandia National Laboratories

Biological/tissue samples present a number of analytical challenges including the detection of trace quantities of high mass species within large (few mm) areas of samples. Recent advances in both ToF-SIMS instruments (such as stage rastering and liquid metal polyatomic ion sources) and data reduction protocol are facilitating biological/tissue analysis. In this poster, we will compare ToF-SIMS spectra and images collected using both Ga (mono-atomic) and Gold 3 (polyatomic) primary ion sources on treated brain tissue sections. Using polyatomic gold we are able to detect and image high mass (> 1,500 amu) species; these species were not detected in the spectra collected using Ga (even with a higher Ga primary ion fluence). The wealth of information contained in spectral images collected using polyatomic gold is tremendous, and the resulting spectral images can be difficult to interpret. In this poster we will also demonstrate that Multivariate Statistical Analysis (MVSA) tools such as AXSIA (Automated eXpert Spectrum Image Analysis) are useful for deconvoluting the spectral images. Using AXSIA, we are able to separate low yield species from high yield species in the high mass (ca. 760 amu) region of the ToF-SIMS spectra. The AXSIA component of this work was funded in part under CRADA SC00/01609 PTS 1609.02 (GE/Sandia). 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.

AS-MoP4 Using ToF-SIMS as a High Throughput Screening Tool for Lightweight Hydrogen Storage Materials, ***J.P. Lemmon***, *J.-C. Zhao, V.S. Smentkowski,* General Electric Global Research Center

Combinatorial Chemistry (CC) coupled with High-Throughput Screening (HTS) techniques are being used at the General Electric Global Research Center to generate and characterize multi-component samples in order to accelerate the discovery of new hydrogen storage materials for automotive applications. In order to meet the DoE target of 6 weight percent hydrogen by the year 2010, the hydrogen storage material must contain low Z (low weight) components. Low Z elements can not be detected using techniques that rely on X-ray generation, such as Electron Probe Microanalysis (EPMA) and/or X-Ray Fluorescence (XRF). ToF-SIMS is ideally suited for the rapid screening of low Z materials since it allows for the detection of all elements and can also image large areas (eg. 70mm x 70mm) in less than 2 hours. ToF-SIMS images can be measured while the combinatorial chemistry library is being heated and/or maintained at the desired temperature in the range of 100 to 600° C. Temperature programmed ToF-SIMS experiments will be used to measure the hydrogen desorption processes of combinatorial chemistry libraries. Select examples will be presented.

AS-MoP5 Comparative Analysis of a Pt/Rh Catalyst Sample with TOF-SIMS and Laser-SNMS, ***A. Schnieders***, ION-TOF USA, Inc.; *F. Kollmer,* ION-TOF GmbH, Germany; *M. Fartmann, H.F. Arlinghaus,* Universität Münster, Germany; *V.S. Smentkowski,* General Electric Global Research Center

In the field of catalysis, the analyst often needs to detect and image the distribution of trace quantities of species within the top most surface layer. Time-of-flight secondary ion mass spectrometry (TOF-SIMS) is a well-established technique for such analysis. Unfortunately, quantitative TOF-SIMS analysis is not always easy to accomplish. Laser postionization of sputtered neutrals (Laser-SNMS) provides a higher sensitivity for many elements than TOF-SIMS, and in case of non-resonant multiphoton ionization (NRMPI), Laser-SNMS also provides for more uniform useful yields over the whole elemental range, thus enabling a more straight-forward way of quantification. In this paper, we compare the use of TOF-SIMS and Laser-SNMS with NRMPI for the analysis of a noble-metal treated stainless steal catalyst sample. The main analytical question focused on the determination of the lateral distribution of Pt and Rh on the surface of an actual (dirty) sample. Despite the relative low sensitivity for Pt, TOF-SIMS analysis enabled the determination of the lateral distribution of Pt and Rh on the surface. Quantification of these metals was possible by normalizing the corresponding ion intensities to those of a matrix signal. In comparison to TOF-SIMS, Laser-SNMS provided higher sensitivities for Pt and Rh as well as for other metals detected on the surface. To obtain accurate quantification, relative sensitivity factors for Pt and Rh were established on control samples. The lateral distributions thus measured confirmed those determined with TOF-SIMS. The similar results obtained with both techniques allowed establishing a procedure for quantification of TOF-SIMS results on similar samples.

AS-MoP6 Application of Time Interpolation to SIMS Isotopic Ratio Measurements, ***D. Simons***, *K.J. Coakley, A.M. Leifer,* National Institute of Standards and Technology

Secondary ion mass spectrometry (SIMS) can be used to perform localized isotopic ratio measurements on a micrometer scale. Such measurements have broad applicability in areas of biology, geology and astronomy. A specific application area of recent interest is nuclear forensics, whereby SIMS has been applied to the search for evidence of uranium enrichment activities through the measurement of the relative abundances of U-235 and U-238 in micrometer-sized particles. In SIMS measurement systems, the count rate of isotopes may vary in time as a limited sample quantity is consumed during the analysis. Since only one isotope at a time is measured in conventional ion counting detection systems, this drift can introduce systematic error into the estimate of the ratio of any two isotopes. Hence, correcting the data for drift is critical to the accurate determination of isotopic ratios and their associated uncertainties. We consider isotopic measurements in a pairwise fashion, with the more abundant isotope of the pair designated as the major isotope and the less abundant one as the minor isotope. We correct the measurements for drift by aligning the major and minor time series of isotopic pairs by use of linear interpolation. We estimate an isotopic ratio for each of two cases. In one case the time series of the more abundant isotope is aligned with respect to the time series of the less abundant isotope. In the second case the less abundant isotope is aligned with respect to the more abundant one. We average both of these estimates to get a drift-corrected estimate. We present an analytical formula for the uncertainty of the isotopic ratio which accounts for correlation introduced by interpolation. We also present an approximate hypothesis test procedure to detect and quantify possible time-dependent drift of the measured isotopic ratio during a single analysis.

AS-MoP7 Carbon Mediation on the Growth of Self-Assembled Ge Quantum Dots on Si (100) by Ultra High Vacuum Chemical Vapor Deposition*, **P.S. Chen,*** Electronics Research & Service Organization, Industrial Technology Research Institute, Taiwan, Republic of China*; S.W. Lee,* Industrial Technology Research Institute, Taiwan*; M.-J. Tsai,* Electronics Research & Service Organization, Industrial Technology Research Institute, Taiwan*; C.W. Liu,* Industrial Technology Research Institute, Taiwan

The growth of self-assembled Ge quantum dots (QDs) with carbon mediation on Si (100) by a hot wall ultra-high-vacuum chemical vapor deposition system with different growth temperatures and surfactant gas flow rates was investigated. The ethylene (C@sub 2@H@sub 4@) and methylsilane (SiCH@sub 6@) gas were as surfactants prior to the growth of Ge QDs, respectively. Small dome-like Ge QDs were observed after carbon treatment as compared to the hut shaped Ge cluster without any carbon pre-treatment at 550 °C. Those dome-like Ge QDs have a mean base width and height of about 40 and 5 nm, respectively, and the density is about 6.7 ï‚´ 10@super 9@ cm@super 2@ at the growth temperature of 550 °C. Comparison with boron mediation, strong Câ?"H bonds during the epitaxy growth play different roles and lead to this dramatic modification of Ge QDs morphologies. Furthermore, multifold Ge/Si layers were also carried out to enhance the emission intensity with first Ge layer treated by C@sub 2@H@sub 4@) and avoid the generation of threading dislocations.

AS-MoP8 Field Emission Analysis and Optimization of Carbon Nanoflake Edge Emitters*, **X. Zhao**, R.A. Outlaw, J.J. Wang, M.Y. Zhu, D.M. Manos, B.C. Holloway,* College of William and Mary

Ultra thin carbon nanoflake (CNF) films have been inductively grown by rf chemical vapor deposition on a variety of substrates. The CNF films grow vertically with respect to the substrate and have flake thicknesses of < 2 nm with terminating edges as small as a single atom layer (graphene). The inordinately high field enhancement factor of the flakes represents a high tunneling efficiency and electron emission. In addition, the packing density of the flakes is also extremely high suggesting that CNF films have great potential as field emission cathodes. To optimize the field emission from these films, the growth conditions, deposition temperature, deposition time and chemical composition were varied. The turn-on field, I-V behavior, noise level, robustness, maximum current density and field emission energy spectra for selected deposition condition were observed. The CNF films were also coated with thin layers of Ti, Zr and Hf and heated to form low work function carbide edges. The resulting characteristics were then compared to uncoated CNF. Adsorption effects of H@sub 2@O and H@sub 2@ for both the uncoated and coated CNF were also studied.

AS-MoP9 Ti Metal Cluster on the Carbon Nanotube*, **S. Lee**, H. Kim, J. Lee, B.Y. Choi, Y.S. Cho, Y. Kuk,* Seoul National University, South Korea

Junctions between metal and carbon nanotube (CNT) have been investigated mainly with transport experiments for the last several years. However, their detailed electronic and geometric structures are not fully revealed. We have created junctions between CNT and Ti metals by depositing the metal on CNT and the electronic and geometric structures have been studied with low temperature scanning tunneling microscopy. Ti metal is preferentially coated near the edges and in the gaps between CNTs. In spatially resolved tunneling spectroscopy, the metallic states are observed on Ti surfaces and the state extended into CNT area, suggesting the existence of mixed states near the junctions@footnote 1@. The origin of the mixed states and observed screening lengths will be discussed. @FootnoteText@ 1) S. Dag, E. Durgun, and S. Ciraci, Phys. Rev. B 69, 121407(R) (2004).

AS-MoP10 Depth Resolution of Inverse Calculation from ADXPS to Depth Profile*, **A. Tanaka,*** Physical Electronics, Japan*; D.G. Watson,* Physical Electronics USA

A practical inverse calculation method is discussed which transforms the data from angle dependent x-ray photoelectron spectra (ADXPS) to depth profile using a maximum entropy method. The depth resolution of the method is evaluated using an 84%-to-16% resolution, which is less than 0.7 nm for natural oxide when optimizing 5 take off angle data. Theoretical comparison is also discussed.

AS-MoP11 Study of the Oxidation Behavior of Aluminum and Aluminum Alloys Using X-Ray Photoelectron Spectroscopy*, G.D. Claycomb, **P.M.A. Sherwood**,* Kansas State University

The oxidation behavior of high purity aluminum and two aluminum alloys, after exposure to a variety of aqueous environments, has been studied by using core and valence band X-ray Photoelectron Spectroscopy. Freshly abraded samples were exposed to de-oxygenated, normal and oxygenated quadruply distilled water for one hour at room temperature, 40Âº, 70Âº and 100ÂºC. For pure aluminum, single oxidized aluminum compounds were formed in some instances while mixtures were formed in other cases. For the alloys, the oxidized aluminum compounds were mixed with oxides of the alloying elements in some instances and in other cases where the films had thickened sufficiently, single oxidized aluminum compounds were found on the outermost surface. Identification of the types of oxides being formed was achieved by using valence band photoelectron spectrum. The spectra were analyzed by using a comparison with the valence band spectra of known oxidized aluminum compounds and spectra generated by additions of the spectra from the known oxidized aluminum compounds together with approaches that used difference spectra. This work is based upon work supported by Luxfer Gas Cylinders.

AS-MoP12 Chemical State Analysis Boron and Phosphorus on Si Wafer Surface Measured by TRXPS*, **Y. Iijima**, T. Tazawa,* JEOL, Japan

It is well known that x-ray photoelectron spectroscopy (XPS) is a meaningful analytical technique for the chemical characterization of material surface, but the detection limit of XPS is inferior to that of other methods, such as secondary ion mass spectrometry (SIMS) and total reflection x-ray fluorescence (TXRF) analysis. Recently, in developing a new DRAM, the energy of P and B injected into an Si wafer was bound to be lowered. Accordingly, the investigation of the chemical bonding states of these elements on the Si wafer surface has become important. Since B1s and P2p photoelectron peaks overlap with the energy loss peaks of Si2s and Si2p peaks, it is difficult to detect a small amount of B and P injected into the Si wafer by XPS. Therefore, the use of x-ray total reflection has become noteworthy in photoelectron spectroscopy. This is because TRXPS (total reflection x-ray photoelectron spectroscopy) can greatly reduce the number of inelastically scattered electrons contributing to the background of photoelectron spectrum, as the effective analysis depth of TRXPS is nearly equal to the x-ray penetration length in the solid. In addition to this, TRXPS is expected to give a lower detection limit. In this work, we examined the chemical bonding state of B and P on the Si wafer by means of TRXPS. In what follows, the effectiveness TRXPS method to the semiconductor surface analysis will be described.

AS-MoP13 XPS Characterization of Ingaalp/ingap Quantum Well Structures*, **Y.J. Yoon**, L.V. Yashina, B.Y. Kim, V. Kureshov,* Samsung Electro-mechanics Co., Ltd, Korea

InGaAlP/InGaP heterostructures are important for light emission in laser diodes. Post growth characterization of InGaAlP solid solution composition is actual problem in the optimization of growth parameters due to compositional dependent mismatch and Eg value. The mismatch is mostly influenced by Ga/In ratio, whereas Eg is governed by Al/Ga ratio. In practice the set of accessible diagnostic procedures is limited by photoluminescence study and XRD. For the quasibinary solid solution composition can be estimated using lattice constant or Eg dependences on mole fraction whereas for the quaternary solid solution this approach can not be applied rigorously. The use of direct analytical techniques is complicated by many factors such as low thickness of layers, restrictions in depth resolution, surface preparation problem. InGaAlP/InGaP multilayered structures with layer thickness ~ 5 nm were studied by XPS. The superlattices were obtained by MOCVD on GaAs(100) substrate. XPS study was carried out using monochromatic Al Ka source in Quantera SXM. Two independent procedures were applied: (1) sputtering depth profiling and (2) Angle dependent photoemission registration for the samples containing well/barrier interface in the layer under analysis. In 3d, Ga 2p, Al 2s, P 2s peak intensities were calibrated using the set of reference alloy samples InGaP, InAlP and pure compounds InP, GaP. Sputtering rate compositional dependence was also taken into account. Sputtering was carried out using Zalar rotation to reach maximal depth resolution. For the depth profiles analysis attenuation length and surface roughness after sputtering, estimated by AFM, were taken into consideration. The obtained results are compared with SIMS data.

AS-MoP14 XPS, AFM, and Confocal Microscopy Data Correlation: Characterization of Polymer Blend Systems to Create a 3D Volume*, **J.L. Fenton**, K. Artyushkova, J. Farrar, J.E. Fulghum,* The University of New Mexico

No single non-destructive technique readily provides both surface chemistry and component distribution through the depth of polymer samples. Visualization based upon multiple analytical characterization techniques can be used to create a 3-D map of polymer chemistry. This work combine data from XPS, AFM, and confocal microscopy analysis of polyvinylchloride/polymethylmethacrylate and polystyrene/polybutadiene blends. Confocal microscopy images are used to create a volume that can be correlated with XPS images and spectra in order to semi-quantitatively map the distribution of chemical components within the blends. The correlated data will be combined with AFM images to incorporate surface topography measurements. This work has been partially supported by NSF CHE-0113724 and the NSF IGERT CORE program.

AS-MoP15 Auger Analysis of Corrosion Scale Formed on a Ni-Cr-Fe Alloy by Exposure to Supercritical Water at Elevated Temperature.*, **S.A. Wight**, J.E. Maslar, E.S. Windsor,* NIST

A nickel-chromium-iron alloy (Inconel 600) was exposed to water at elevated temperatures and pressures (approaching conditions of the critical point of water). This alloy is used in boiler systems and the mechanisms of corrosion and failure are of interest. The water temperatures and pressures were selected to simulate conditions to which this alloy might be exposed during operation. Two coupons were exposed under slightly difference conditions and differences in degree of corrosion were observed. While the alloy composition is well known, the composition of the corrosion layer depends strongly on exposure conditions. Auger electron spectrometry was applied to help investigate the composition of the corrosion layer. The discontinuous nature of the oxidation layer and the proximity to the unoxidized substrate make this a challenging analysis. Auger analysis is complimented with energy dispersive spectrometry, and focused ion beam techniques to solve this complicated analysis problem.

AS-MoP16 Electronic Structure of Rare-Earth Oxoborates: A Photoemission Investigation*, **A.J. Nelson**, J.J. Adams, K.I. Schaffers,* Lawrence Livermore National Laboratory

Calcium's rare-earth (R) oxoborates are nonlinear optical materials with general composition Ca@sub 4@RO(BO@sub 3@)@sub 3@ (R@super 3+@ = La, Sm, Gd, Lu) that have potential for high-average power laser frequency conversion and intra-cavity doubling. X-ray photoemission was applied to study the valence band electronic structure and surface chemistry of these novel materials and their rare-earth oxide model compounds. Core-level and valence band results for the rare-earth oxides La@sub 2@O@sub 3@, Sm@sub 2@O@sub 3@, Gd@sub 2@O@sub 3@, and Lu@sub 2@O@sub 3@, were applied to the interpretation of the photoemission spectra of select oxoborate crystals. Specifically, high resolution photoemission measurements on the La and Gd 3d and 4d, Ca 2p, B 1s and O 1s core lines and valence band were used to evaluate the surface and near surface chemistry of lanthanum calcium oxoborate (LaCOB) and gadolinium calcium oxoborate (GdCOB). Results for these oxoborate crystals revealed that the occupied states exhibit a high degree of mixing between the p-f bonding-antibonding states. In addition, general treads in the 3d and 4d core-level line shapes and occupied 4f valence band states of the rare-earth oxide model compounds are best understood in terms of final state effects. 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.

AS-MoP17 Photoelectron Spectroscopy Study of the Aging and Plasma Treatments Effects on PECVD a-SiC:H Films for Advanced Interconnects*, **V. Jousseaume**, O. Renault,* CEA-DRT-LETI, France*; G. Passemard,* ST-Microelectronics, France

The ageing of amorphous hydrogenated SiC (a-SiC:H) films grown by PECVD and used as potential low k dielectric barrier materials in advanced interconnects was investigated by x-ray photoelectron spectroscopy. Very thin layers (20-60 nm) and a special sample holder were used in order to minimize detrimental charging effects during analysis. It is shown that ageing on non-treated films proceeds by the introduction of up to 20at.% of oxygen into the film after 15 days of air exposure in the clean room, and that O is present in relatively high concentration at the very early stages of air exposure@footnote 1@. By XPS is evidenced the benefits of both He and H2 plasma treatments in term of drastic limitation of the reoxidation upon ageing, with an atomic percentage of O being stable at around 7at.% after 15 days. At the same time, on untreated samples, the Si/(Si+C) ratio is remaining constant and both Si2p and C1s core-level profiles show up a constant evolution as a function of ageing time, with a decrease of the relative intensity of Si-C bonds and an increase of oxycarbide and C-C, C-H groups. This evolution will be compared with the case of plasma treated samples and possible mechanisms of ageing will be proposed taking into account results from FTIR analysis, stress and dielectric constant measurements@footnote 2@. @FootnoteText@ @footnote 1@McCurdy et al., J. Electrochem. Soc., 145-9 (1998) 3271).@footnote 2@Jousseaume et al., E-MRS Meeting 2004.

AS-MoP18 Thermally Nitrided Stainless Steels for Polymer Electrolyte Membrane Fuel Cell Bipolar Plates: Beneficial Modification of Passive Layer on AISI446*, **H.M. Meyer III**, M.P. Brady, K.L. More, B. Yang,* Oak Ridge National Laboratory*; H. Wang, J.A. Turner,* National Renewable Energy Laboratory

Proton exchange membrane fuel cells (PEMFCs) are of great current interest for power generation due to their high efficiency and environmentally friendly, near-zero emissions. Since cost is critical, metal alloys would be ideal as bipolar plates but suffer from inadequate corrosion behavior due to high electrical resistance by the formation of surface oxides or degrade cell performance by contaminating the membrane with metal ions. Recently, it was discovered that thermally grown Cr nitrides (CrN/Cr2N) on a model Cr-bearing alloy, Ni-50Cr (wt%), show great promise for corrosion resistance and electrical conductivity in PEMFC bipolar plate environments @fototnote 1@. Work is ongoing to form similar nitride surfaces on less expensive Ni-Cr and Fe-Cr base alloys. This poster describes an effort to use a relatively inexpensive ferritic stainless steel (AISI446 MOD-1) as bipolar plate material and specifically looks at its surface chemistry, corrosion resistance, and interfacial contact resistance. Thermal nitridation for 2 h at 1100ÂºC resulted in little nitrogen uptake and a tinted surface. Analysis by SEM, XPS, and AES suggests a complex heterogeneous modification of the native passive oxide film by nitrogen, rather than the desired micron range thick exclusive Cr-rich nitride layer. Surprisingly, this modification resulted in both good corrosion resistance under simulated cathodic and anodic conditions and low ICR, well over an order of magnitude lower than the untreated alloy@footnote 2@. Details of the nitrided surface chemistry of this alloy will be presented. @FootnoteText@ @footnote 1@ M.P. Brady, K. Weisbrod, I. Paulauskas, R.A. Buchanan, K.L. More, H. Wang, M. Wilson, F. Garzon, L.R. Walker, Scripta Materialia, 50(7) pp.1017-1022 (2004).@footnote 2@ H. Wang, M P. Brady, K.L. More, H.M. Meyer III, and J. A. Turner. Submitted to Journal of Power Sources.

AS-MoP19 Preparation and Lithography of Monolayers on Silicon Surface and Their Molecular Recognition*, **Y. Takahashi**,* Waseda University, Japan*; N. Shirahata,* National Institute for Materials Science, Japan*; A. Hozumi,* National Institute of Advanced Industrial Science and Technology, Japan*; S. Asakura,* Waseda University, Japan*; T. Yonezawa,* University of Tokyo, Japan

Functionalization of hydrated silicon surface is a starting stage in the development of molecular, biomolecular and semiconductor devices. Refluxing of 1-alkene under nitrogen with H-terminated Si gives an uniform Si-C linked monolayer with atomically flatness through thermal hydrosilylation. We have reported that the monolayer can be prepared from a dilute solution of 1-alkene (< 1 wt%) and even from powder of 1-alkene molecules. This basic finding that the monolayer can be prepared from the powder implies that solid materials, including those with exceedingly high melting points or no melting points, have the potential to be transformed into monolayers directly bonded to inorganic substrates, with the only limitation being that the material must be soluble into any kinds of solvents. The carbohydrate monolayer recognizes the specific protein molecules selectively. Lithography of such monolayer can be done by UV-light irradiation. Furthermore, the particle monolayer of alkenethiol-stabilized gold nanoparticles were also be anchored onto silicon by similar reaction. These findings will promise that individual nanoscale materials can be manipulated based on monolayer formation mechansm.

AS-MoP20 Importance of Binding Energy Reference Materials for Understanding the Chemistry of Oxidized-Iron Arsenic-Adsorbing Materials*, B.M. Sass,* Battelle Columbus*; **M.H. Engelhard**, D.R. Baer,* Pacific Northwest National Laboratory

Arsenic as a contaminant in drinking water is a growing problem around the world. Consequently many research and commercial efforts are being made to develop low cost and effective means for producing acceptable quality drinking water. Iron oxide based sorbing minerals are now available commercially. However, the effectiveness, lifetime and ability to recycle these materials are not adequately understood. The extent of arsenic sorption and the chemical nature of the sorbed species are important to understanding the chemistry that take place on the surface and the long term effectiveness. We have used XPS to measure the arsenic coverage on the mineral surfaces and to examine arsenic chemical state. Because of the limited amount of arsenic oxidation state data in general, the variability of binding energies observed in the existing data, and the lack of data for arsenic sorbed onto oxidized iron phases, to interpret our data it was necessary to examine As(III) and As(V) oxides as well as ferric arsenite and ferric arsenate compounds. Based on these references the arsenic sorbed onto the commercial sorbers was found to be mostly As(V) in the conditions examined.

AS-MoP21 Analysis of Leed Images to Obtain Surface Geometries of Amines and Alcohols Adsorbed on the Si(100)-2x1 Surface, ***J.K. Dogbe***, *S.M. Casey,* University of Nevada, Reno

Image analysis of low-energy electron diffraction (LEED) intensity vs. voltage (IV) curves was used to analyze the surface geometries of amines and alcohols adsorbed on the Si(100)-2x1 surface. Clean silicon and ammonia-covered surfaces were used as calibration systems. The data from these surfaces compare well within experimental uncertainties. Results to be presented include the dimethylamine, trimethylamine and ethanol-covered surfaces. These results will be compared to computational treatments of probable reaction pathways of these adsorbates on silicon using the cluster models of the surface. Also to be presented will be comparisons of results for these reactions from slab models of the surface.

AS-MoP22 Surface Planarization Characteristics of WO3 Thin Film for Gas Sensing, *W.S. Lee,* ***P.J. Ko***, Chosun University, South Korea; *Y.J. Seo,* DAEBUL University, Korea, South Korea

There has been an increasing interest in the material and electrical properties of inorganic compound that are insulators at low temperature, but are good conductors at high temperature. In particular, n-type semiconductors such as SnO2, WO3, TiO2 and ZnO have extensively been used for detecting reduction gases. For the applications of gas sensors, it is necessary to have a microstructure with small grain size yielding large ratio of the surface area to the bulk. Also, the surface roughness deteriorates light reflection, pattern resolution, and device performance because they are dependent on surface morphology or roughness. Therefore, it is important to control the microstructure and surface morphology for the advanced sensor application. Chemical mechanical polishing (CMP) process is a useful guideline for improving the surface roughness. In this paper, we investigated the CMP effects on the surface morphology of WO3 thin films prepared by RF sputtering system. In order to compare the polishing characteristics of WO3 thin film, we discussed CMP removal rate (RR) and within-wafer non-uniformity (WIWNU%), particle size distribution, and the microstructures of surface and cross-sectional layer by atomic force microscopy (AFM) analysis. And the effects of added oxidizer contents on the WO3 CMP characteristics were investigated to obtain the higher removal rate and lower non-uniformity. This work was supported by a Korea Research Foundation grant (KRF-2002-005-D00011).

AS-MoP23 Scanning Capacitance Microscopy Study on the Stability of the Electrical Junctions Formed by Spike Annealing and Rapid Thermal Annealing, ***M.-N. Chang***, *C.-Y. Chen,* National Nano Device Laboratories, Taiwan

Scanning capacitance microscopy (SCM) has been widely used to profile two-dimensional carrier distribution and examine the electrical junctions of silicon-based devices. Ion implantation combined with proper annealing treatments is indispensable to produce a needed electrical junction. In general, the annealing treatments can be rapid thermal annealing (RTA) or spike annealing (SA) at high temperature. Due to the photoperturbation effects on SCM, there are many difficulties in employing SCM to investigate the temperature influence on electrical junctions. In this work, we have provided a reliable method to control the photoperturbation levels on the studied samples and employed low-photoperturbed SCM, operated under the same photoperturbation levels, to study the stability of the electrical junctions formed by RTA and SA. Studied samples were p@super +@/n junctions formed by BF@sub 2@@super +@ implantation at low energies. RTA and SA processes were performed at 1050 °C in N@sub 2@ ambient. The width and pitch of the designed grating pattern are 0.8 and 2 @micro@m, respectively. The differential capacitance images clearly show that post-SA and -RTA furnace annealing at low temperatures can induce the electrical junction narrowing. With secondary ion mass spectroscopy, it is further revealed that the junction narrowing may occur even if atomic diffusion is negligible. The experimental results indicate that point defect generation/recombination associated with dopant deactivation plays an important role of junction width modification during the following low temperature processes. According to this study, the electrical junction formed by high temperature annealing is unstable. The physical mechanism of junction width variation induced by low temperature processes will be discussed in depth.

AS-MoP24 XPS Analysis Under External Stimuli, ***S. Suzer***, *U.K. Demirok, G. Ertas,* Bilkent University, Turkey

Earlier, we demonstrated that, by applying external voltage bias to the sample rod while recording XPS spectra, it was possible to influence the measured binding energy differences by controlling the partial charging/discharging of different surface layers or domains either by electrons created from a filament, or by stray electrons within the vacuum system stemming form X-ray tube, vacuum gauges, etc.[1, 2]. We had used this to separate otherwise overlapping XPS peaks belonging to different surface features.[3] Later, we expanded it to extract time-dependent information. [4] In this contribution, we will present our extended investigation of different surface structures like Au nanoclusters deposited on SiO2 substrates or thin organic layers of various thickness, etc., using different external voltage stimuli over other external elements like resistors, capacitors for extracting information related with the dielectric properties of surface structures and probing nanocluster-surface interactions. @FootnoteText@ [1] B. Ulgut, and S. Suzer, J. Phys. Chem. B 107, 2939 (2003). [2] F. Karadas, G. Ertas, and S. Suzer, J. Phys. Chem. B 108, 1515 (2004). [3] S. Suzer, Anal. Chem. 75, 7026 (2003). [4] U. K. Demirok, G. Ertas, and S. Suzer, J. Phys. Chem. B 108, 5179 (2004).

Biomaterial Interfaces
Room Exhibit Hall B - Session BI-MoP
Poster Session

BI-MoP1 Immobilization of Avidin on COOH-modified SiO@sub 2@/Si(100) Surface and Characterization by AFM and BML-IRRAS, ***N. Misawa***, *S. Yamamura,* The Graduate University for Advanced Studies, Japan; *T. Urisu,* Institute for Molecular Science, Japan

Nowadays bio-mimetic sensing techniques, using immobilization of intact biomolecules on solid surfaces, attract significant attentions. For solid substrates, silicon is a suitable material since precise micro-fabrication has been established. New biosensors can be combined with electronics devices on the same chip. Characterizations by IR spectroscopy and AFM observation are useful tools to investigate biomolecules immobilized on silicon surface. It is known that BML-IRRAS (Infrared Reflection Absorption Spectroscopy using Buried Metal Layer substrate [1]) is a high-resolution surface vibration spectroscopy on the semiconductor or insulator materials, which has sub-monolayer sensitivity for the wide frequency range including fingerprint regions. In this study we have immobilized avidin, which has high versatility for conjugation of biomolecules with solid surface, on the SiO@sub 2@/Si(100) surface modified with carboxyl group, and characterized the surfaces by AFM and BML-IRRAS for the first time. The -COOH modification was produced by the deposition of 2-(carbomethoxy) ethyltrichlorosilane and sequential hydrolysis by HCl. Immobilization of avidin was performed after condensation reaction by N-hydroxysucciniimide and EDC, which enhanced the reactivity of carboxyl group with amino group of avidin. AFM images showed that the roughness of the -COOH modified surface was less than 0.5 nm, and protrusions with about 15 nm diameter and 2 nm height appeared after the avidin immobilization. The BML-IRRAS measurements showed clear peaks at 1650 cm@super -1@ and 1550 cm@super -1@, which were assigned to Amide I and Amide II bands of avidin. These bands also consisted of several fine structures which might be assigned to secondary structures such as @alpha@-helix and @beta@-sheet etc. The detailed shape analysis of these bands could give the information with orientations of these immobilized proteins. [1] S.Yamamura. et al. Jpn. J. Appl. Phys. 42 3942 (2003).

BI-MoP2 An Application of Microcantilever for Biosensor using Piezoresistivity, ***K.H. Na***, *C.J. Kang, Y.S. Kim,* Myongji University, Korea

A microcantilever-based biosensor with piezoresistor has been fabricated using surface micromachining technique that allows a simple fabrication procedure and a low cost sensor. A microcantilever integrated with piezoresistive readout enables sensing even for non-transparent liquids such as blood and miniaturizing the size of biosensor compared with optical readout. Adsorptions of bio-chemical species on a functionalised surface of a microcantilever will cause surface stress. This makes microcantilever bending and results in the change of the resistance of piezoresistor in the microcantilever. The structural layer of the microcantilever is fabricated with LPCVD silicon nitride film and the sacrificial layer is LPCVD polysilicon film. The cystamine terminated with thiol was covalently immobilized on the gold-coated side of the microcantilever. The immobilization process was characterized by measurement of the microcantilever deflection in real time monitoring. We are going to present a cantilever deflection after a formation of cystamine/glutaraldehyde/protein-A/anti-protein-A composite layers and to measure a limited resolution of the cantilever-based biosensor for a concentration of biomolecule.

BI-MoP3 Architectured Surfaces for On-Probe Affinity Capture MALDI Mass Spectrometry, *G.R. Kinsel,* ***Z. Segu****, R.B. Timmons,* University of Texas at Arlington

MALDI MS is a powerful analytical tool for the characterization of proteins and peptides and is presently used extensively for the analysis of biomolecules extracted from biological media. In these applications one or more purification / fractionation steps are typically required prior to MALDI MS analysis. The development of affinity fractionation approaches performed directly on the MALDI probe is considered attractive because of shortened analysis time, inherent simplicity and reduced sample loss. However, a significant challenge for these on-probe affinity fractionation approaches is the limited capacity of the MALDI probe surface. The significance of protein solution concentration, surface-protein binding constant, and total protein surface capacity, with respect to the MALDI limit of detection for a given protein in a mixture, is revealed in theoretical studies utilizing the systematic treatment of equilibria. Additional experimental studies confirm the predictions of the theoretical model and reveal the importance of the MALDI probe capacity on protein detection using modified probes. In addition, a novel method to increase the capacity of modified MALDI probes is presented. In this approach gold particles are attached to allyl amine RF plasma polymer modified MALDI probes and subsequently modified to incorporate affinity capture ligands through the attachment of biotinylated alkane thiols. Preliminary data demonstrates that these modified gold bead attached MALDI probes allow the selective capture of targeted biomolecules and offer significant increases in the biomolecular binding capacity of the MALDI probe surface.

BI-MoP4 Single Nanoparticle Detection of Biological Molecules via Darkfield Microscopy, ***G. Nusz****, A. Chilkoti,* Duke University

Noble metal nanoparticles have been used as sensors for biological molecules because of their unique interactions with light due to the resonant collective oscillations of the conduction electrons known as surface plasmon resonance (SPR). The frequency at which this resonance occurs is strongly dependant upon the dielectric constant of the medium surrounding the particles. We have previously shown that gold nanoparticles chemisorbed on to glass and subsequently functionalized with a biological receptor can optically transduce analyte binding at the surface of the nanoparticles. This is because when the target analyte binds to the receptor functionalized nanoparticles, the dielectric constant of the surrounding media increases, resulting in a measurable shift of the SPR frequency that can be measured as a color change. In this study, we report the extension of this label free optical biosensor to single nanoparticles that are chemisorbed onto glass. Gold nanoparticles in the size range of 13-40 nm and gold nanorods (30 nm diameter, aspect ratio 2.7) are synthesized in solution. The nanoparticles are chemisorbed on to the surface of an amino-terminated silane monolayer under conditions that result in sparse coverage of the nanoparticles on the substrate. Darkfield microscopy is used to detect the SPR shift of a single nanoparticle by analyzing its scattering spectrum as a function of the change in the dielectric constant in the vicinity of a single nanoparticle. Applying this technique to a single nanoparticle offers the advantage of effective detection of a target analyte with detection limits on the order of a few hundred molecules.

BI-MoP5 Development of Organic Semiconductors Using Metal Doped Fish Protein, ***T. Arockiadoss,*** Central Leather Research Institute, India*; F.P. Xavier,* LIFE, Loyola College, India*; B.K. Prabhu, M. Babu,* Central Leather Research Institute, India

Bioelectronics is an emerging field, which extensively uses the supra-molecular structure of proteins, DNA etc to evolve products applicable in biosensors, switchable membranes, organic thin film transistors and fuel cells. This study shows that a partial purified metal-doped muscle protein from the fish, Clarius battracus, was fabricated with poly vinyl alcohol (PVA) to form a biopolymer thin film. The initial protein characterisation was done by gel electrophoresis, followed by analysing the thin film, using circular dichorism, fourier transformed infrared spectrum, scanning electron microscopy, electrical conductivity with and without temperature dependency and finally cyclic voltameter was used to study the architectures of donor and acceptor molecules. The study concludes that the metal-doped fish muscle protein and PVA gives rise to a conducting biopolymer, leading to a versatile molecular electronic material having a unique electrical and optical property, which could be used as a semiconductor in the arena of biochip, fuel cell and nanotechnology. @FootnoteText@ KEY WORDS: FISH, CONDUCTIVITY, METAL DOPING, PROTEIN.

BI-MoP6 Biocompatibility of Microelectronic Materials*, H.D. Wanzenboeck,* ***C. Almeder****, E. Bertagnolli,* Vienna University of Technology, Austria*; E. Bogner, M. Wirth, F. Gabor,* University Vienna, Austria

Cell-based biosensors endeavor to use microelectronic data acquisition and processing to evaluate specific signals from living cells. The potential of these bioelectronic sensors has been recognized for numerous applications in medicine, pharmaceutical research, environmental diagnostics and the food and processing industries. The interaction between living tissue and microelectronic materials is the critical issue for all those systems, as the inorganic material must neither interfer with nor harm the cells. The effects of different microelectronic materials on the growth of human colon carcinoma cells have been investigated. A systematic study of the survivability and the growth of an exemplary cell culture on various materials used in microelectronics was performed. The viability and the adhesion of colon carcinoma cells (Caco-2) was tested on 15 different materials - metals, dielectrics and semiconductors - commonly used in microelectronics fabrication. Growth inhibiting materials such as copper and blank gallium arsenide have been identified as well as highly biocompatible materials such as silicon, silicon nitride, chromium and gold. Cells have also been cultured on a microelectrode array consisting of metal and dielectric materials on the same substrate. Neither the sub200 nm height step nor the change of the material showed to effect the cell growth. Several materials have been successfully tested to facilitate the growth of cell structures. The results allow a versatile application for microelectrode arrays and demonstrates the wide compatibility of semiconductor technology for fabrication of cell-based biosensors.

BI-MoP7 The Use of Novel Self-Assembled Monolayers for Enhancing Biosensor Performance*,* ***W. Laureyn****, F. Frederix, K. Bonroy, T. Ghoos, R. De Palma, K. Jans, C. Zhou, G. Reekmans,* IMEC, Belgium*; P. Declerck, W. Dehaen, G. Maes,* KULeuven, Belgium*; C. Van Hoof,* IMEC, Belgium

The increasing miniaturisation of biochips and the demand for higher sensor detection sensitivities put severe demands on the process and methodology of coupling biomolecules to surfaces. More specifically, controlled thin film structures have to be created which allow the bio-affinity elements to be arranged and addressed in a reproducible and controlled manner. Addressing these issues, IMEC has developed promising methodologies for the construction of novel, well-defined biosensor interfaces, based on the deposition of Self-Assembled Monolayers (SAMs) of alkane thiols or disulfides on metal (e.g. gold) and alkyltrichlorosilanes on oxide (e.g. tantalum pentoxide) surfaces. In addition, polymeric biosensor interfaces have been created on gold using grafted polysiloxane-g-poly(ethylene glycol) polymers. In order to retain biological activity and to allow for the necessary accessibility, the biomolecular functional units have been immobilised onto gold and oxide surfaces derivatised with mixed SAMs. In the mixed SAM approach, the first molecule carries a functional group to firmly attach the bioreceptor molecule and the second molecule resists the non-specific adsorption of undesired biological entities. Different types of mixed SAMs have been optimised, containing e.g. molecules with a molecular backbone comprised of protein-resistant functionalities and molecules with highly reactive functional moieties. For protein detection, mixed SAMs were optimised in order to increase the amount of receptor molecules (antibodies and fragments) on the surface, while still mitigating non-specific adsorption, allowing for highly sensitive immunosensing in non-specific matrices. For the detection of small molecules, highly reproducible and tuneable immobilization protocols were developed, based on mixed SAMs. The optimisation of these (mixed) SAMs was conducted using various surface characterisation tools and using SPR and QCM-D for immunosensing experiments.

BI-MoP8 Surface Modified MALDI Probes for Affinity Fractionation of Protein Mixtures*, G.R. Kinsel,* ***M. Li,*** *G. Fernando, L. van Waasbergen, R.B. Timmons,* University of Texas at Arlington

Matrix assisted laser desorption/ionization mass spectrometry (MALDI-MS) has become a powerful analytical tool for the characterization of proteins. As the effectiveness of the MALDI method has advanced, the need for high-speed separation and purification of peptides/proteins in complex mixtures (e.g. culture media, serum or urine) has increased. The approach described in this presentation focuses on the use of RF plasma polymer coated MALDI probes as platforms for peptide and protein separation based on their hydrophobicity. Pulsed RF plasma deposition of allyl alcohol directly on the MALDI probe surface is used to produce surfaces with various hydrophobicities. Control of the degree of the hydrophobicity is achieved through changes in the duty cycle of the pulsed RF plasma. Testing of the surfaces for peptide/protein separation based on their hydrophobicity is performed using various laboratory prepared control mixtures and mixtures obtained from biological sources. In all cases fractionation of the protein/peptide mixture was evaluated through the acquisition MALDI mass spectra using a Bruker AutoFLEX MALDI TOFMS or a laboratory-constructed linear MALDI TOFMS. Data has been obtained from surfaces with different hydrophobicities that demonstrate the efficacy of these modified MALDI probe surfaces for achieving on-probe fractionation of peptide/protein mixtures.

BI-MoP9 Micropatterned Substrate Screening under Shear Flow (MiSSUS): Direct Comparison of Receptor-ligand Binding*,* ***K.A. Burridge,*** *M.A. Figa, J.Y. Wong,* Boston University

Microfluidic patterning has been combined with a parallel plate flow chamber to enable screening of combinatorial variations in targeted drug delivery carrier surface properties under tunable physiologically-relevant shear conditions. Carriers containing either drugs or imaging agents must have surface properties that promote binding to targets yet at the same time block rapid immune system clearance. In addition, ligand-receptor mediated attachment must overcome shear flow in the vasculature which decreases contact times and applies forces on bonds. Patterned bilayers which mimic the surface of liposomal delivery vehicles are created by injecting pre-mixed vesicle solutions into lanes formed by a polydimethylsiloxane stamp reversibly sealed to a glass slide. After removing the stamp in an albumin solution to form protein barriers that prevent bilayer expansion, the slide is assembled into a flow chamber for binding studies. MiSSUS provides direct quantitative comparison of the effects of variations in ligand architecture such as relative molecular weights of liganded and unliganded polyethylene glycol. Experiments using MiSSUS revealed that ligand spacer length is an important factor in maintaining adhesion under flow, i.e. that longer spacers confer higher detachment resistance.

BI-MoP10 Microfluidic Circuit Fabrication and Packaging for Surface-Controlled Bioprocesses in BioMEMS*, T.M. Valentine,* ***J.J. Park,*** *G.W. Rubloff, R. Ghodssi,* University of Maryland

We have previously demonstrated that biopolymers (specifically, the polysaccharide chitosan) can be deposited in vitro at patterned, voltage-programmed electrodes, and that subsequent coupling and conjugation of biomolecules (proteins, nucleic acids) opens the door to applications such as bioassays and enzymatic catalysis. To extend these capabilities beyond simple devices to more complex bioMEMS systems, robust means for microfluidic circuit fabrication and packaging are required. We have designed and fabricated microfluidic networks to support combinatorial test site libraries for surface-controlled bioprocesses, along with packaging approaches to control fluidics and electrical inputs/outputs to the bioMEMS systems, with emphasis on robust technologies for leak-free microfluidics, use of polymer-based MEMS, incorporation of electrode structures and optical access to them, and reliable exchange of bioMEMS systems through reusable packaging which allows rapid connection of fluid and electrical inputs/outputs to external control systems. Three different approaches to microfluidic design, based on both sealing and bonding, are promising in concert with the packaging strategy. The efficacy of these fabrication and packaging approaches is demonstrated through results on fluidic sealing and on the electrically programmable deposition of NHS-fluorescein labeled chitosan at internal sites in the bioMEMS system. The impact of flow rates and residence times on biopolymer deposition and biomolecular conjugation reflect key chemical engineering questions associated with surface bioreactions in microfluidic systems, laying the groundwork for future applications in miniaturized bio-reactors and chemical and biological sensors.

BI-MoP11 Near-Field Interaction of Infrared Radiation with an Atomic Force Cantilever*,* ***E.S. Gillman,*** NanoSpec Corporation

Infrared vibrational spectroscopy is a powerful tool for chemical identification, however most infrared spectroscopic techniques usually do not obtain spatially resolved chemical information at a nanoscopic level due to the fact that they are diffraction limited. On the other hand, a scanning near-field optical microscope (SNOM) can reveal features with spatial resolution less than the diffraction limit because it relies on near-field probing instead of optical focusing. Using an apertureless approach that is based on atomic force microscope (AFM) cantilever tip ineracting with a infrared source of sufficient intensity, spatially resolved chemical information as well as conventional topographic information can be obtained. Critical to this is the near-field interaction of the AFM cantilever tip and the surface in the presence of an electromagnetic field. Modeling of this interaction will show that this approach can result in parctical device for nanoscale chemical imaging.

BI-MoP12 Nanoscale Chemomechanical Patterning of Silicon and Germanium Surfaces Using an Atomic Force Microscope*,* ***R.C. Davis,*** *M. Tonks, K. Barnett, M. Lee, M.R. Linford,* Brigham Young University

In nanoscale chemomechanical patterning, an atomic force microscope (AFM) probe is used to scribe a flat silicon surface under a solution of reactive molecules, attaching a layer of the molecules to the scribed line. This technique was previously used to functionalize silicon surfaces using a moderate range of scribing forces (5 µN to 80 µN). Here we will present a study focusing on the smaller forces (1µN to 5 µN) on both silicon and germanium surfaces resulting in significantly reduced tip wear and yielding lines down to 20 nm wide. We will also present the extension of chemomechanical patterning to include the attachment of proteins to the functionalized lines.

BI-MoP13 Force Spectroscopy of Mechanically Stretched Fibronectin*,* ***K.L. De Jong,*** *P.R. Norton, N.O. Petersen,* The University of Western Ontario, Canada

Cell motility is a delicate balance between adhesion and detachment. Identifying key proteins involved (for example, fibronectin, Fn) and understanding the mechanisms employed to find this balance, will provide new insight into the means by which motility can be controlled. Mechanical forces play a key regulatory role in biological cells, and therefore to understand how cells move and adhere, ultimately relies on knowledge of how forces are generated and propagated or in essence, how the cell interacts with the surface. The stress on Fn fibres may be the deciding factor in determining the attachment of the cell to the matrix, and the adhesion of the matrix to the substrate. Studies geared toward understanding fibronectin structure, organization, and binding affinity under mechanical stretching, are providing information crucial to the understanding of the effect of mechanical forces on cell function. To test the prediction that stretching Fn reduces integrin-binding activity, an AFM compatible device is designed to apply a mechanical force to fibronectin while the change in intermolecular interactions that result is monitored. The force required to rupture the interaction between an integrin mimic and fibronectin is determined to be approximately 100 pN. After stretching fibronectin, a trend towards fewer rupture events characterized by smaller pull-off forces in each force curve is observed; this implies a decrease in potential binding sites available to the integrin mimic and concomitant weaker interactions.

BI-MoP15 Plasma Polymerization of Tetraglyme for PEO-like Surfaces and Plasma Immobilization of PEO Surfactants for Improved Blood Compatibility*,* ***J.L. Lauer,*** *J.L. Shohet, R. Muguresan, R.M. Albrecht,* University of Wisconsin-Madison*; U.H. von Andrian,* Harvard Medical School*; S. Esnault, J.S. Malter,* University of Wisconsin-Madison*; S.B. Shohet,* University of California, San Francisco

The realization of small scale biomedical devices will be closely related to the non-fouling/biocompatibility properties of the exposed surfaces and the uniformity of the surface treatment throughout the device. PEO and PEO-like surfaces are significantly advantageous in preparing medical devices that require good blood compatibility. In this work, we explore two plasma process techniques, plasma polymerization (PP) and plasma immobilization (PI), to improve the blood compatibility of various polymer and non-polymer surfaces. Thrombus formation and embolization are significant problems for blood-contacting biomedical devices. To minimize these affects, plasma polymerized tetraethylene glycol dimethyl ether (tetraglyme) was deposited on flat Si3N4, and SiO2 samples to produce a PEO-like surface coating. In addition, a microplasma was used to immobilize a Poly(ethylene oxide) (PEO) surfactant to the lumenal surface of PE and PTFE tubing (ID 1.14mm). A microwave-cavity diagnostic was used to measure the plasma density of the microplasma inside of the polymer tube. Emitted light from the plasma during the PP and the PI processes was fed into a monochromator. Coating thickness and chemical composition of the flat surfaces was measured using ellipsometry and XPS, respectively. Contact-angle measurements were made for both the flat PP surfaces and the PI polymer tubes. To test blood compatibility, both the flat PP surfaces and the PI polymer tubes were exposed to heparinized human blood. After blood exposure, the tubes were examined with a scanning electron microscope to assess the density of adhering platelets on the flat PP surfaces and along the length of the PI polymer tubes. The plasma-treated surfaces showed fewer blood adherents than the untreated surfaces. By suitably modifying the plasma parameters, the treatment for both plasma processes can be optimized.

BI-MoP17 Nonfouling Microstructures on Hydroxylated Substrates via Chemical Vapor Deposition and Surface Initiated Atom Transfer Radical Polymerization*, **H. Ma**, A. Chilkoti,* Duke University

The ability to covalently modify hydroxylated substrates such as glass and metal oxides with a non-fouling polymer coating is an important goal, in view of their wide application as biomaterials and in biotechnology. Most current approaches rely upon physisorption of PEG-containing polymers or grafting of the polymers from solution to the surface (â?ografting toâ?⍰ approach). We report here a â?ografting fromâ?⍰ strategy in which an oligo(ethylene glycol) functionalized monomer is polymerized in situ from the surface of glass to provide high-density polymer brushes that overcomes the intrinsic limitation of low surface density of PEG chains realized by â?ografting toâ?⍰ strategies. A silane initiator presenting a terminal bromoisobutyrate moiety was used to form a SAM on hydroxylated substrates via chemical vapor deposition (CVD). This SAM was used as substrate for surface initiated atom transfer radical polymerization (SI-ATRP) of oligo(ethylene glycol) methyl methacrylate (OEGMA). The SI-ATRP was carried out in an oxygen free environment with CuBr/bipyridine as catalysts in a water /methanol mixture. Poly(OEGMA) brushes with a tunable thickness between 2 and 10 nm can be synthesized in situ, and these brushes are exceptionally resistant to protein adsorption, even from 100% fetal bovine serum. We also report a new masking strategy to pattern the surface with the initiator silane SAM, which enabled facile patterning of the surface with the poly(OEGMA) brushes. When NIH 3T3 fibroblasts were seeded onto those surfaces, cells were confined within the regions demarcated by the polymer and were maintained within the pattern for over a week.

BI-MoP18 Plasma Grafted Anti-Fouling Films on Ethylene Oxide Base for Biosensors and Biotechnologies*, **M. Kormunda**, G. Ceccone, A. Papadopoulou, M. Hasiwa, F. Rossi,* EU-JRC-IHCP, Italy

The generation of anti-fouling surface is a key element in the design of biosensors, medical devices and implants. Protein adsorption resistant surfaces have to avoid or reduce non-specific protein adsorption, platelet adhesion and thrombus formation, to prevent undesirable responses of the living systems to the device. The highly cross-linked anti-fouling coatings on ethylene oxide base were plasma grafted from Dimethoxydiethylene glycol vapour in mixture with reactive (N@sub 2@) or inert (Ar) gas at low-pressure 40mTorr. The plasma discharge in capacitive configuration of reactor was powered by continuous (from 10 to 100W) or pulsed RF (13.56MHz) voltage. The coatings were plasma grafted on glass, Si and PTFE substrates placed on grounded substrate holder. The film chemical composition has been analysed by XPS and FTIR as well as the surface morphology (AFM) and the protein adsorption (QCM-D). The coatings toxicity and an adhesion of Fibroblast L929 have been investigated on selected samples. The lower power plasma grafted coatings have very good antifouling properties together with low receding contact angles although the methyl function groups in the films are more populated than ethylene oxides groups. The coatings are stable with low contact angles over period about 6 months at normal conditions. No significant changes were observed on functional groups in coatings washed for 40 days in ethanol bath. The oxygen plasma etching during a nano-patterning process for biosensors fabrication has not significant influence on chemical composition, surface morphology and contact angles.}

BI-MoP19 Local Property of Linear Plasmid DNA on the Metal Wires with Different Potential*, **S.H. Jin**, J.M. Son, N.J. Lee, C.J. Kang,* Myongji University, Korea

Linear plasmid DNA crossed on the patterned nano metal wire is characterized by scanning capacitance microscopy and electrostatic force microscopy. The metal wires processed on the silicon wafer followed by a capping thin dielectric film were used as a local potential source for the DNA molecule. By varying the voltage bias applied to the metal wire, initial stage of DNA deposition on the substrate is observed and local electrical properties, such as capacitance variation and change of surface potential are measured. With images and spectroscopy, we investigate DNA moleculeâ?"substrate interaction.

BI-MoP20 Analysis of Contaminants in Commercial Thiolated Single-stranded DNA Oligomers by XPS and ToF-SIMS*, **C.-Y. Lee**, L.J. Gamble, D.G. Castner,* University of Washington

Commercially produced thiolated single-stranded DNA (SH-DNA) molecules are used in a variety of biotechnology applications including biosensors and DNA microarrays. The diversity of techniques used by different vendors in the synthesis and treatment lead to a significant variation in the quality of SH-DNA. In this work, we used x-ray photoelectron spectroscopy (XPS) and time-of-flight secondary ion mass spectrometry (ToF-SIMS) to perform a comparative study of the relative purity of commercially-available SH-DNA from several vendors. We find that thiol-terminated 16-base pair oligomers from two of the vendors, which were self-assembled as thin layers onto gold surfaces, contain excess carbon and sulfur. By using ToF-SIMS, several contaminants including poly(dimethylsiloxane) (PDMS), lipid molecules, and sulfur-containing molecules were identified by their molecular fragments. Preliminary ToF-SIMS data indicates that the excess sulfur arises from the reductant (dithiothreitol) used to purify the SH-DNA by some of the vendors. Time dependent studies of purified versus contaminated SH-DNA were performed to determine the effect of contamination on DNA surface assembly over time. XPS results of purified SH-DNA show increased P, N, O and C atomic percentages over a 24-hour time period, confirming increasing DNA surface coverage on the gold. In contrast, XPS results of contaminated SH-DNA show that C and O atomic percentages increased over time, but no increase was observed in the P and N. This indicates that, after the initial SH-DNA adsorption during the first five minutes, the excess material adsorbed for the rest of the 24 hours was due to contamination.

BI-MoP21 Empirical Force Field Evaluation for the Molecular Simulation of Protein Adsorption*, **V. Raut**, S.J. Stuart, R.A. Latour,* Clemson University

Molecular simulation provides a direct method to theoretically investigate the molecular mechanisms governing the adsorption behavior of proteins to biomaterials surfaces. Because of their size, empirical force field based methods must be used for these types of simulations. Force fields (ffs), however, must be parameterized for specific molecular systems. While ffs have been designed to accurately represent the behavior of proteins in solution, none have considered peptide-surface adsorption behavior in their parameterization. Therefore, there is currently no basis to support the accuracy of simulation results. The objective of this research was to develop computational methods to complement our previous experimental studies that measured the adsorption free energy (G*) for a host-guest peptide on Au-alkanethiol self assembled monolayer surfaces (SAMs), and to use these methods for ff evaluation. Host-guest peptides were modeled in the form of SGSG-X-GSGS, where G=glycine, S=serine, and X=any selected peptide type. Molecular dynamics simulations were conducted using the GROMACS ff to calculate G* for these peptides over functionalized SAMs (CH3, OH, NH2, COOH, PEG) in a 40@Ao@ x 40@Ao@ x 60@Ao@ simulation cell with explicit solvation (water with Na+ and Cl-ions) contained within periodic boundary conditions. While simulation results for certain peptide-SAM systems are generally in agreement with experiments, others show substantial deviations from expected adsorption behavior. Parameter modifications of this ff are thus required for this application. Further work is planned for the eventual development of a validated ff for protein adsorption simulations.

BI-MoP22 Investigation of the Binding Mechanism of the Bacterial Adhesin Scp to Fibronectin*, **J.R. Hull**,* The University of Washington*; D.G. Castner,* University of Washington*; G. Tamura,* Children's Hospital and Regional Medical Center

Several pathogens bind specifically to immobilized fibronectin (Fn), and not to soluble Fn, including Group B Streptococci (GBS), S. pneumoniae, S. sanguis, and p-fimbriated strains of E. coli. However, the structural basis for the specific adherence of Scp to immobilized Fn has not been resolved. There are two possible mechanisms for Scp binding to Fn. First, specific conformational determinants of Fn that allow Scp binding may be unmasked when Fn is immobilized. Second, Scp may bind to a combinatorial determinant formed by the clustering of multiple immobilized Fn molecules. The Scp-Fn binding interaction is being studied with two complementary analysis methods. Surface Plasmon Resonance (SPR) is being used to study the kinetics of the binding interactions and

Atomic Force Microscopy (AFM) is being used to investigate single molecule interactions. Supporting experiments to determine surface compositions was done using X-ray Photoelectron Spectroscopy. SPR has shown that the binding affinity of soluble Scp to adsorbed Fn is approximately nano-molar and that Scp does not bind soluble Fn. A model system was set up to develop AFM methods for examining the Scp-Fn interactions. Collagen related peptides (CRPs) on the AFM tip were used to interact with adsorbed Fn. The CRPs were attached to the AFM tip via homo-functional N-hydroxysuccinimide (NHS) poly(ethylene glycol) (PEG) cross-linker. The jump heights of the force distance curves were graded based on Studen@aa t@s t-test and only events with a nominal grade were further analyzed. Analysis of unbinding events shows that there are multiple interactions centered at 75 pN and there are multiple length scales over which these interactions occur. There are at three length scales over which these interactions occur: 5 nm which is attributable to nonspecific adhesion, 15 nm which is the NHS-PEG spacer length, and 30 nm and greater which is attributable to CRP-Fn interactions.

BI-MoP23 L-Cysteine Adsorption on Cu(100) Studied by Sulfur K-edge NEXAFS and XPS*, **S. Yagi**, Y. Matsumura, T. Nomoto,* Nagoya University, Japan*; J.A. Syed, S.A. Sardar,* Hiroshima University, Japan*; K. Soda,* Nagoya University, Japan*; E. Hashimoto, M. Taniguchi,* Hiroshima University, Japan

For the application to medical materials it is important to study the mechanism of reaction at interface between amino acid, which is the component of protein, and metal, and the influence of water on the mechanism. We have paid attention to L-Cysteine [HSCH@sub 2@CH(NH@sub 2@)COOH] and investigated the adsorption behavior of L-Cysteine/Cu(100) by Sulfur K-edge Near Edge X-ray Absorption Fine Structure (NEXAFS) and X-ray Photoelectron Spectroscopy (XPS) techniques. Sulfur K-edge NEXAFS spectrum for L-Cysteine/Cu(100) shows that the main peak of @sigma@@super *@(S-C) is decreased in comparison with the spectrum for L-Cysteine powder. This means that L-Cysteine molecule obtains some electrons from the Cu(100) surface.

BI-MoP24 Orientation of a Y-shaped Biomolecule Adsorbed on a Charged Surface*, **Y.-J. Sheng**,* National Taiwan University, Taiwan, ROC*; H.-K. Tsao,* National Central University, Taiwan*; S. Jiang,* University of Washington

The adsorption and orientation properties of a Y-shaped biomolecule, which models an immunoglobulin (Ig), on a charged surface are analyzed mesoscopically by Monte Carlo simulations. The orientation is a consequence of the interplay between van der Waals interactions and electrostatic interactions. For adsorption dominated by van der Waals attraction, the molecule prefers lying flat on the surface. For weak attraction, we observe a depletion zone in the concentration profile, which can result in a negative surface excess. A secondary peak is found for strong adsorption. For electrostatically dominated adsorption, the orientation is mainly determined by electric dipole and a vertically adsorbed molecule can be attained as it possesses strong electric dipole. Our study provides an explanation for experimental observations of preferential orientation.

BI-MoP25 Interfacial Dynamics of a Gelatin Solution with Surfactant*, **H.-K. Tsao**,* National Central University, Taiwan*; S.-Y. Lin,* National Taiwan University of Technology, Taiwan

In terms of dynamic surface tension, the interfacial dynamics of gelation solutions with various surfactants are investigated by pedant bubble tensiometry. On the basis of local equilibrium assumption, the thermodynamics of dynamic surface tension is analyzed. The adsorption efficiency of gelatin is low compared to that of small surfactant. However, the surface activity of gelatin may be enhanced due to intrachain and interchain rearrangement at the interface, which results in long relaxation time signature. The interplay between adsorption efficiency and surface activity categorizes our experimental results into two types of dynamic behavior. For type I dynamics, the gelatin molecule is completely displaced from the interface and the interfacial dynamics is dominated by that associated with surfactant. Nevertheless, the interaction of gelatin with surfactant in the bulk solution can alter the surfactant surface excess and hence the surface tension. For type II dynamics, the gelatin molecule is partially displaced from the surface and the dynamics displays a long relaxation characteristic. The extent of surface tension decrement due to gelatin conformational change manifests the degree of gelatin displacement from the interface. Our conclusion is able to elucidate the peculiar dynamic surface tension of a solution of gelatin and PEG.

BI-MoP26 Detergency Effectiveness with Respect to Proteins*, **M. Richard**, T. Le Mogne,* Ecole Centrale de Lyon, France*; J. Criquelion,* Laboratoires Anios, France*; A. Perret-Liaudet,* Hopital Neurologique de Lyon, France*; J.M. Martin,* Ecole Centrale de Lyon, France

In the detergency field of re-usable medical devices, a special attention is focused on the non-conventional transmissible agent called prions which is a proteinaceous infectious agent. Few cleaning procedures are effective against prions and few techniques are available to study cleaning effectiveness with respect to proteins in general. The first part of our study shows that X-ray Photoelectron Spectroscopy (XPS) is a useful and reliable technique to evaluate detergent formulations effectiveness to remove proteins from stainless steel surface soiled with a human brain homogenate. A semi-quantitative evaluation of the detergency effectiveness could also be performed. XPS makes it possible to study chemical species remaining on surface, substrate properties after cleaning procedures and also the water quality effect on detergency effectiveness. In the second part of our study and in the light of the complexity of the previous system, a simplification of each part of the system was carried out. XPS analysis was used to study the effectiveness of some simple chemical functions to remove proteins from a native oxide layer of a pure chromium surface. The results will be presented and discussed in this paper.

BI-MoP27 Reflex-Arc on a Chip: an in Silico Cell Culture Analogue*, **K.A. Wilson**, M. Das, L.C. Riedel, C.A. Gregory, M. Poeta, D. Damjanovich, P. Molnar, J.J. Hickman,* Clemson University

To date understanding of and development of therapies for traumatic spinal cord injury (SCI) and neurodegenerative diseases have been problematic due in part to difficulties associated with the various models used to test new drug therapies. Animal studies are expensive, time consuming, and raise ethical issues. In vitro studies are less expensive and avoid many of the ethical issues associated with animal studies, but are often poor predictors of human response. To overcome the shortcomings of existing models we are developing a microscopic cell culture analogue (microCCA) of the spinal reflex-arc. This system should retain the cost effectiveness of in vitro systems while allowing complex tissue interactions and environmental dynamics that more realistically reflect the in vivo state. The present work draws on advances in a wide variety of technical fields including cell culture, surface chemistry, and microfabrication. These advances have allowed us to begin development of a microCCA device comprised of the basic components of the reflex-arc: a muscle fiber, a dorsal root ganglion (DRG) cell, and a motoneuron. Silicon microstructures serve as the foundation of the device. Surface modification with alkyl-silane SAMs followed by patterning with deep UV photolithography was performed to selectively control cell adhesion and growth. XPS analysis indicated monolayer formation. Furthermore, we have demonstrated the control of neuronal growth and myotube differentiation on the microstructures. Electrophysiology results have confirmed that the neurons and myotubes have physiological properties consistent with previous findings. With this system it will ultimately be possible to report on a variety of properties of the reflex-arc, thereby creating a cost-effective, predictive test bed for the development of novel drug therapies for traumatic SCI and a wide variety of neurodegenerative diseases.

BI-MoP28 Compartmentalized Bioreactor for Long-Term Culture of Bone Cells*, **R. Dhurjati**, E.A. Vogler, P.W. Brown, H.J. Donahue,* Pennsylvania State University

A compartmentalized bioreactor designed around the concept of continuous growth and dialysis, was used to study long-term (15-30 days) phenotypic behavior of human fetal osteoblastic cells (hFOB). This specific design separates the growth and feeding functions and permits long term culture sustaining the pericellular environment, otherwise disturbed by continuous or punctuated growth medium replacement. The attachment and growth behavior of model human osteoblasts cultured in the bioreactor was evaluated using scanning and transmission electron microscopy (SEM/TEM) and were compared to those obtained from conventional tissue culture methods. Results suggest that stable culture conditions afforded by the reactor has enhanced utility in the long-term culture of osteoblasts in terms of growth, proliferation and mineralized matrix deposition characteristics and would serve as an ideal in-vitro test system for the study of cell/protein mediated interactions with synthetic bone analog materials.

BI-MoP29 Cell-Surface Interactions between Marine Diatoms and Fouling-Release Coatings Studied with Atomic Force Microscopy*, **P.F.M. Terán Arce**, R. Avci,* Montana State University*; I.B. Beech,* University of Portsmouth, UK*; K.E. Cooksey, B. Wigglesworth-Cooksey,* Montana State University

Interactions between marine microorganisms, and fouling release coatings are of major significance to the Navy and maritime industry. This interaction usually occurs by means of adhesive exopolymers (EPS) secreted by the microorganisms, which allow them to attach and settle on different surfaces. In the present study, viable marine diatom cells were immobilized on tipless AFM cantilevers and used as bioprobes to investigate the adhesion forces between exopolymers, produced by the immobilized diatoms, and surfaces of Intersleek (@super TM@ International Paints) elastomers. These forces, as well as the work exerted against them, were statistically compared with the forces between the same diatoms and mica surfaces. In spite of the dissimilar character of Intersleek (hydrophobic) and mica (hydrophilic) surfaces, comparable results were obtained on both. Force vs distance curves on both surfaces presented several adhesion peaks with force magnitudes that ranged from hundreds of pNs to tens of nNs and polymer elongations up to several microns. These results demonstrate the ability of diatoms to produce hydrophobic and hydrophilic exopolymers.

BI-MoP30 Development and Characterization of RGD Peptide Coatings for Cell Adhesion*, **R. Canteri**, C. Pederzolli, L. Lunelli, P. Villani, L. Pasquardini, M. Vinante, G. Speranza, S. Forti, M. Anderle,* ITC-irst, Italy*; J.J. Park, G.W. Rubloff,* University of Maryland

The development of biomaterials able to modulate the interaction of mammalian cells with solid substrates is important for many applications, e.g., tissue replacement/regeneration and substrates for cell culture. A common mechanism that mediates cell adhesion involves the interactions between integrin receptors on the surface of mammalian cells and ligands of adhesive proteins present in extracellular matrices (ECM) and bloodstream. These proteins include fibrinogen, fibronectin, vitronectin, collagen, laminin, Von Willebrand factor. It has been demonstrated that the adhesive domains comprise a short peptide sequence, Arg-Gly-Asp (RGD), the most important recognition site for about half of all known integrins. This work describes a three-step reaction procedure for coupling a six-amino-acid (GRGDSY) fibronectin fragment synthesized with an additional cysteine (C) at the C-terminus, to solid substrates. The first step is the activation of the substrate with an amine layer, introduced by chemical modification (silanization) or by using an amino-containing biopolymer (chitosan). In a second reaction step, N-hydroxysuccinimidyl (NHS) ester polyethylene glycol (PEG) is grafted to the aminated surfaces. Fluorescence quantitative showed 1-5 x10@super 13@ PEG molecules/cm@super 2@ immobilized on the surface. The distal end of these PEG molecules carry two possible chemical groups: a maleimide or a vinylsulfone group, both selectives for reaction with sulfhydryl groups. The final step is the covalent attachment of RGD-containing peptides on the resulting terminal PEG derivatives. XPS, ToF-SIMS, AFM, SEM, fluorescence spectroscopy and microscopy were applied to characterise the surface. The RGD modified surfaces were tested using different cell lines. The results obtained on the functionalized surface showed an higher extent of cell adhesion, with mainly round-shaped cells at the initial stage of the spreading, compared to the non-modified surface.

BI-MoP31 Characterization of Nuclear Impalement by Vertically Aligned Carbon Nanofibers for Gene Delivery*, A.V. Melechko,* University of Tennessee, Knoxville*; **T.E. McKnight**, G.D. Griffin, D.K. Hensley, M.J. Doktycz, D.H. Lowndes,* Oak Ridge National Laboratory*; M.L. Simpson,* Oak Ridge National Laboratory, University of Tennessee

Penetration of DNA-modified vertically aligned carbon nanofibers (VACNF) into live cells provides efficient delivery and expression of exogenous genes, similar to â?~microinjectionâ?T-styled methods, but on a massively parallel basis. The efficiency of this method however depends on many factors including plasmid coverage on each nanofiber, maintaining transcriptional activity of these plasmids following immobilization, and retention or release of plasmid from the VACNF scaffold during and after insertion into cell. For DNA that remains tethered, it is believed that gene expression occurs if plasmid is delivered not only into intracellular domain but moreover into nuclear domain. In this work we report on a study of insertion and residence of VACNFs into the nuclei of mammalian cells (Chinese hamster ovary) using Laser Scanning Confocal Microscopy and Scanning Electron Microscopy.

BI-MoP32 Deposition of Lipid Bilayers on the Silicon Dioxide Surfaces Patterned by Focused Ion Beam and Synchrotron Radiation Etching*, **R. Tero**,* Institute for Molecular Science, Japan*; M. Rahman,* The Graduate University for Advanced Studies, Japan*; Z.-H. Wang,* Nagoya University, Japan*; M. Sugawara,* Nihon University, Japan*; K. Nagayama,* National Institute for Physiological Sciences, Japan*; T. Urisu,* Institute for Molecular Science, Japan

Nano-bioelectronics is one of the most attractive research fields in these days. Microfabrication and modification with biomaterials on solid surfaces have fascinated enormous attentions as important techniques for the development of new biosensors and new devices. We have fabricated fine structures on SiO@sub 2@/Si surfaces by combination of the focused ion beam (FIB) and the synchrotron radiation (SR) etching, and deposited lipid bilayers on the SiO@sub 2@ surface by the vesicle fusion method. FIB patterning was performed using JEOL-JFIB2300 with the 30 keV of Ga ion. SR etching was performed in the BL4A2 in UVSOR in IMS using Co photomask with the thickness of 400 nm under the mixture gas of SF@sub 6@ and O@sub 2@ (P@sub SF6@=5.0x10@super -2@ Torr, P@sub O2@=2.0x10@super -3@ Torr). AFM images were obtained by Picoscan (Molecular Imaging). In the deposition of lipid bilayers, the sample was incubated above the gel-liquid crystal transition temperatures in the suspension of the pure dipalmitoylphosphatidylcholine (DPPC) or the mixture of egg PC, dioleoylphosphatidylethanolamine (DOPE) and cholesterol (3:1:1), which were prepared by agitating the vacuum-dried lipid films in a buffer solution. We have patterned the Co photomask on the SiO@sub 2@/Si substrate by FIB in micrometer order. Three-dimensional micrometer-order structures were successfully obtained by one time SR irradiation (2.0x10@super 4@ mA min). After deposition of DPPC vesicles on the SiO@sub 2@ surface, flat membranes with the height of 5 nm were observed by atomic force microscopy (AFM). The thickness of the membranes well corresponded to that of the single lipid bilayer. The morphology, electronic resistance and additional effect of protein (gramicidin A) will be discussed.

BI-MoP33 Interfacing Natural and Synthetic Biomaterials: Development of a Multilayered Vascular Scaffold*, E.J. Taschner, J.B. Leach, **J.Y. Wong**,* Boston University

One of the greatest challenges in designing functional small diameter vascular grafts is to mimic key arterial mechanical properties (e.g., strength and compliance). Our hypothesis is that the underlying scaffold organization is a crucial factor in cellular remodeling, and ultimately, the mechanical properties of biologic vascular grafts. Thus, the overall goal of our research is to develop a multilayered or lamellar vascular scaffold biomaterial that more closely mimics the organization of native artery extracellular matrix. Our approach is to seed vascular smooth muscle cells between layers of poly(lactic-co-glycolic) (PLGA) thin films and naturally derived hydrogels (e.g., collagen, fibrin). However, the major challenge to the creation of such a multilayered scaffold is to promote stability and adhesion between the hydrogels and the relatively hydrophobic PLGA films. Therefore, to promote adhesion between the composite layers, the PLGA films were surface modified to contain specific highly reactive groups. First, the PLGA films were treated in NaOH to expose surface carboxylic acid and alcohol groups. Then, carbodiimide-mediated reactions were used to covalently bind photoreactive moieties to the PLGA films as well as the hydrogel precursor monomers. The film-cell-hydrogel composite constructs were assembled and then exposed to ultraviolet light to initiate the photopolymerization. We tested the adhesion between the layers using a modified peel/creep test that applied a constant "peel" force over time. The modified PLGA composites were associated with a significant amount of resistance to the peeling force while the unmodified PLGA controls failed instantaneously. We therefore demonstrate a promising method of creating stable, multilayered tissue scaffolds from composites of natural and synthetic biomaterials.

BI-MoP34 Immobilization of the Enamel Matrix Derivate Protein Emdogain onto Polypeptide Multilayers as studied by in situ Ellipsometry and QCM-D*, **T.J. Halthur**,* Royal Institute of Technology, Sweden*; I. Slaby, A. Lindeheim,* Biora AB, Sweden*; P. Claesson,* Royal Institute of Technology, Sweden*; U. Elofsson,* YKI AB, Institute for Surface Chemistry, Sweden

The build-up of the biodegradable poly(L-glutamic acid) (PGA) and poly(L-lysine) (PLL) multilayers on silica and titanium surfaces, with and without an initial layer of polyethyleneimine (PEI), was investigated and characterized by means of in situ ellipsometry and Quartz Crystal Microbalance with Dissipation (QCM-D). A two-regime build-up was found in all systems, where the length of the first slow growing regime is dependent on the structure of the initial layers. In the second fast growing regime, the film thickness grows linearly while the mass increases more than linearly (close to exponentially) with the number of deposited layers. The film refractive indices as well as the water contents, indicate that the film density changes as the multilayer film builds up. The change in film density was proposed to be due to polypeptides diffusing into the multilayer film as they attach. Furthermore, the use of PEI as initial layer was found to induce a difference in the thickness increments for PGA and PLL. Comparisons between ellipsometry and QCM measurements revealed that the multilayer film was highly hydrated (as much as 70-75% water) and might therefore serve as a good template for proteins and cells. The hydrophobic aggregating Enamel Matrix Derivatives (EMD) protein Emdogain was successfully immobilized both on top of as well as within the multilayer structures while measured in situ with ellipsometry and QCM and in vitro with ELISA. These polypeptidemultilayer/EMD films are thought to be able to trigger cell response and induce biomineralization and might therefore be used as bioactive and biodegradable coatings for future dental implants.

BI-MoP35 In-situ Formation of Bioactive-Titanium Coating using Reactive Plasma Spraying*, M. Inagaki,* *Y. Yokogawa, T. Kameyama,* National Institute of Advanced Industrial Science and Technology (AIST), Japan

A surface modification technique using reactive plasma spraying (RPS) was studied to form bioactive-titanium (Ti) coating. An in-situ surface-modification of Ti particles is conducted by making use of plasma-enhanced reactions between the Ti particles and the reactive gaseous species in the plasma flame during plasma spraying. Surface-modified Ti coatings were deposited on Ti substrates by radio-frequency (rf)-RPS using a thermal plasma of Ar gas containing 1-6% N@sub 2@ and/or 1-6% O@sub 2@ at an input power of 16 kW. As a means of surface modification, Ti powders impregnated with 0.05-0.2 mol% Ca were also sprayed. Compositional changes in the coatings' surface after soaking in simulated body fluid (SBF) were examined by Fourier transform infrared spectroscopy (FT-IR) and thin film X-ray diffraction (TF-XRD). The Ti coatings prepared with Ar-O@sub 2@ and Ar-N@sub 2@-O@sub 2@ plasma formed apatite after 3 days of soaking in SBF. This indicated that such coatings have the ability to form a biologically active bone-like apatite layer on their surface. In the TF-XRD patterns for the Ti coatings sprayed with oxygen-containing plasma, minute peaks ascribable to TiO@sub 2@ (anatase and rutile phase) were commonly observed. On the other hand, no compositional change was observed in the surface of the Ti coatings sprayed with Ar-N@sub 2@ plasma, even after 7 days of soaking in SBF. In SBF tests, we observed a retardation of apatite deposition for the Ca-added Ti coatings prepared with Ar-O@sub 2@ and Ar-N@sub 2@-O@sub 2@ plasmas. Analyses by X-ray photoelectron spectroscopy indicated that the Ca impregnated in the RPS-Ti coatings formed a Ca-O compound.

BI-MoP36 Effects of He, Ar Ion Implantation on the Surface Chemistry and Structure of Biomedical Polymers*, M. Manso Silvan,* Institute for Health and Consumer Protection, European Commission, Italy*; A. Valsesia, M. Lejeune, D. Gilliland, G. Ceccone, F. Rossi,* Joint Research Centre, European Commission, Italy

Ion beams have become during the last years an outstanding tool for the processing of biomedical devices due to their ability to modify the structural and chemical properties of polymers. The surface chemistry, determinant factor in the performances of biosensor and tissue engineering devices, can be tailored by exposure to ion beams in different ranges of energies and ion doses. Regarding the case of noble gas implantation (Ar, He) at energies from 25 up to 100 KeV, we have found that the surfaces of biomedical polymers such as Polymethylmethacrylate (PMMA), Polystyrene (PS), Polycaprolactone (PCL) and Polyethyleneglycol (PEG) can be notably modified by exposure to doses below 10@super 14@ cm@super -2@. These transformations were applied to adapt the polymer stability in aqueous media or the surface activity towards protein attachment. A series of physico-chemical characterization tools were used in order to follow the surface and structural changes related to the implantation conditions. Fourier transformed infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS) and time of flight secondary ion mass spectroscopy (ToF-SIMS) were used to monitor compositional changes of the implanted samples before and after interaction in biomolecular assays at protein and peptide level. Atomic force microscopy (AFM) and Ellipsometry revealed topographic and structural changes while contact angle and Zeta potential measurements evidenced changes in the molecular interaction of the polymers surface. In particular, it is shown that relevant modifications can be observed in polymer samples exposed to identical ion doses but with beams characterized by different ion density.

BI-MoP37 Plasma Sterilisation of Thermalabile Materials*, H. Halfmann***,** *M. Schulze, M. Czichy, P. Awakowicz,* Ruhr-Universitaet Bochum, Germany

In recent years plasma sterilisation has been developed to a certain degree that makes the corresponding results reliable. Due to the advantages of plasma sterilisation great efforts in world wide investigations are made. The dry and cold process without toxic ingredients is the large benefit of the plasma sterilisation. At the institute of Electrical Engineering and Plasma Technology (AEPT) investigations on plasma sterilisation of medical implants and PET are performed. The experiments are focused on spores and germs which are important in medical, pharmaceutical and food branches. Additionally the influence of the plasma treatment on pyrogens is examined. With the sterilisation and surface modification our attention is on medical implants made of titan, UHMWPE and degradable polylactide. Conventional procedures have several disadvantages besides the long total treatment time. The plasma process reduces germs by 6 decades in a total treatment time of less than 2 minutes. Unlike common sterilisation processes the procedure is also able to reduce pyrogens. In addition to the sterilisation the surface of UHMWPE is hardened by the plasma process. Gel content measurements indicate the improvement of abrasion resistance while the bulk material is not modified. An increasing part of non-carbonated and non-acidic beverages have been bottled in PET. For sensitive products aseptic filling must be guaranteed. A plasma process prepares bottles for aseptic filling within seconds without toxic residua. To improve the shelf-live of oxygen-sensitive soft drinks a diffusion barrier made of a SiO@sub x@ layer can be deposited on the inner side of a PET bottle in a second process step. The whole process may be performed on a plasma line microwave reactor and is done in less than 10 seconds. The future work is aimed at unterstanding the mechanisms of sterilisation in the plasma with regard to ions, neutrals and radicals to optimise the procedure.

BI-MoP38 A Scanning Small Angle X-Ray Scattering (SAXS) Study of the Nanometer Length Scale Bone Structure in Connection with Implants*, M. Foss,* *M.H. Bunger, K. Erlacher,* University of Aarhus, Denmark*; L. Haisheng, Z. Xuenong, B.L. Langdahl,* Aarhus University Hospital, Denmark*; F. Besenbacher, J.S. Pedersen,* University of Aarhus, Denmark

The understanding of the interaction between bone and orthopaedic implants is important for the development of biomaterials with improved biocompatibility. The SAXS technique has previously been applied to offer structural information on mean crystal thickness, predominant orientation and degree of orientation of mineral particles in bone. Therefore, one possible application of SAXS is to investigate the nanostructure of bone in connection with ingrowth on implants, which is not possible with conventional optical techniques. Three sections of pig vertebrae with a thickness of 190µm were examined. One sample included the neurocentral growth zone, while the other two were sections with bone and pieces of either titanium or tantalum implants. Bone provided a strong SAXS signal and relatively low transmission intensity, whereas regions within the neurocentral growth zones showed a high transmission as well as a high SAXS signal. Combining the transmission and the SAXS data, it was possible to differentiate between areas of fibrous tissue and bone. This was supported by elemental analysis performed by SEM-EDAX. The mineral particles in the cancellous bone were aligned along the trabeculae, with less orientation close to the growth zone. Also, the mineral particles tended to be aligned along the implant surfaces. Within the individual bone samples, a large variation in all SAXS parameters were observed depending on the bone position relative to the implant. Furthermore, larger particle thicknesses were found in areas of bone formation, which matches our growth zone data. The data suggests that the parameters obtained by SAXS can be used to assay the local mineral particle growth. This indicates that SAXS is a powerful tool for the characterization of the detailed mineral structure of bone in the vicinity of implants.

BI-MoP39 Photoacoustic Analysis of Bone Osteogenesis to Different Doses of Irradiation Laser*, P. Lomelí Mejia,* IPN SEPI-ESIME, Mexico*; J.L. Jiménez Pérez,* CICATA-IPN, Unidad Legaria, Mexico*; A. Cruz Orea,* CINVESTAV-IPN, Mexico*; G. Urriolagoitía Calderón, L.H. Hernández Gomez,* IPN SEPI-ESIME, Mexico*; H. Lecona Butron,* Centro Nacional de Rehabilitación y Ortopedia, Mexico

The photoacoustic analysis of fractured bone callus to different consolidation times in presence of the irradiation laser, was performed. In this study we take into account the fractured tibias of sacrified Wistar rats. By using photoacoustic spectroscopy (PAS) technique it was possible to determine, for different doses of laser irradiation (doses from 5 to 10 Jcm-2) the presence of characteristic absorption peaks of p-Nitrophenylphosphatase (p.Npp) in the fractured bone callus. The evolution of bone consolidation was accelerated by laser radiation when compared with non irradiated fractures bones.

Dielectrics
Room Exhibit Hall B - Session DI-MoP
Poster Session

DI-MoP1 Surface Preparation for Atomic Layer Deposition of High-K Oxides on Silicon Studied by XPS and SPM*, **J.M. Sturm**, A.I. Zinine, H. Wormeester, R.G. Bankras, J. Holleman, J. Schmitz, B. Poelsema,* University of Twente, The Netherlands

Atomic Layer Deposition (ALD) is regarded as a suitable deposition technique for high-K metal oxides. In order to obtain a good interface quality with the silicon substrate, preparation of the starting surface is of major importance. The initial stage of Al@sub 2@O@sub 3@ deposition from trimethylaluminium and water and growth of thin films (~ 5 nm) were studied by XPS and SPM techniques. XPS was used to determine the growth rate and chemical state of the interface and deposited film as a function of wet-chemical pre-treatment of the starting surface and the pulse time of precursor and purge pulses. Ambient AFM showed that the deposited films are microscopically rough, with a correlation length of typically 20 nm and without correlation on larger length scales. UHV STM was used to investigate the stability of a hydrogen terminated Si surface in vacuum at typical growth temperatures of 250-300 °C used in ALD growth. Starting surfaces with a high RMS roughness of about 0.6 nm resulting from a concentrated HF dip did not change significantly by annealing at pressures below 5x10@super -10@ mbar. However, annealing in a higher background pressure of 3x10@super -8@ mbar (mainly H@sub 2@O) as typically present in a deposition set-up was found to result in a decrease of the surface roughness. These results indicate the importance of in-situ preparation of the starting surface and characterization of its chemical stability.

DI-MoP2 Orientation Selective Epitaxy of CeO@sub 2@ Thin Films on Si(100) Substrates by Magnetron Reactive Sputtering Enhanced by Oxygen Radical Beams with Substrate Bias*, **T. Inoue**, M.O. Ohashi, N. Sakamoto, S. Shida,* Iwaki Meisei University, Japan*; T.W. Chiu, K. Yamabe,* University of Tsukuba, Japan

It is found that the epitaxial CeO@sub 2@(100) and CeO@sub 2@(110) layers are able to be selectively grown using reactive dc magnetron sputtering enhanced with an inductively coupled rf plasma (helicon sputtering) by controlling substrate bias and plasma power.@footnote 2@ Although many reports have been made on the growth of CeO@sub2@(110)/Si(100), recently CeO@sub 2@(100) layers have been reported to grow on atomically cleaned Si(100) surfaces with a 2x1 reconstructed structure in an ultra-high vacuum. Our method has superiority in the requirement of only practical H-terminated surfaces obtained by the usual wet cleaning process. Adopting 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, the CeO@sub 2@(100) layer epitaxy is attained applying adequate substrate bias whereas CeO@sub 2@(110) layers are grown without substrate bias. Helicon sputtering is performed at rf power of 50 W for helicon chathode coil, 120 W for helicon chathode dc plasma power and substrate bias ranging between -20 and +50 V. 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. 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, beyond which (110) layer grow. Precise mapping of growth paramters, 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 improve crystalline quality and to lower the epitaxial temperature, we have started to develop a novel reactive sputtering method employing oxygen free radical beams. The oxygen radical source is operated typically under the conditions; applied rf power of 50 W and O@sub 2@ gas flow of 1 sccm, whereas the intensity of free radical beams is varied controlling rf power and oxygen gas flow. We demonstrate the experimentsl results indicating its effectiveness; successful epitaxial temperature lowering and crystalline quality improvements. Chracterization of the epitaxial films are carried out using RHEED, 4-circle XRD, XTEM and AFM, including C/V and I/V measurements for getting fundamental electrical properties. This orientation selective epitaxial growth technology will be useful for device applications. @FootnoteText@ @footnote 1@ Present address: ULVAC-PHI Corp., 370 Enzou, Chigasaki 253-0084, Japan@footnote 2@ T. Inoue et al., J. Vac. Sci. Tehcnol. A 22(1), 46 (2004).

DI-MoP3 Characteristics of Mo@sub x@Si@sub y@ Gate Electrodes for Advanced CMOS Applications*, **P. Sivasubramani**, P. Zhao, I.S. Jeon,* University of Texas at Dallas*; J. Lee, J. Kim,* Kookmin University, Korea*; M. Kim, B.E. Gnade, R.M. Wallace,* University of Texas at Dallas

Metal gates have been investigated to overcome several challenging issues such as poly-depletion and B penetration for conventional poly-Si gates. Recently, the dual metal gate approach has attracted attention to improve CMOS performance, as opposed to mid-gap metals, such as TiN and TaN. For CMOS integration, tunable metals may be suitable for metal gate applications. Alloying and implantation are being considered as possible techniques to tune the metal gate workfunction. In particular, silicidation is an acceptable process for Si IC fabrication. In this study, we investigated the characteristics of the Mo-Si alloy system for dual metal gate applications. Mo has been demonstrated as a possible P-MOS gate metal because of its high work function and good thermal stability. In this presentation we focus on the tunability of work function, thermal stability and electrical characteristics of Mo silicide as a function of Si concentration. Mo silicide has three different stable silicide phases, Mo@sub 3@Si, Mo@sub 5@Si@sub 3@ and MoSi@sub 2@. Mo silicide samples were prepared on SiO@sub 2@ on Si wafers. The samples were annealed by RTA for 15sec. up to 1000°C. We observed metal work function tuning of at least 0.5V by changing the composition. We also found a possible thermal instability issue of MoSi@sub 2@, even at room temperature. The dependence of characteristics on composition will be discussed based on XPS, XRD, RBS, TEM, CV and IV results. This work is partially supported by the TATP (Texas Advanced Technology Program) and COSAR (Collaborate Project for Excellence in Basic System IC Technology-Korea).

DI-MoP4 TiN/Ta@sub 2@O@sub 5@/PE-SiN/TiN MIM Capacitor for RF and Mixed Signal IC Applications*, **Y.S. Chung**, K.S. Kim, Y.S. Ryu, S.B. Hwang, C.-S. Shin,* Hynix Semiconductor Inc., Korea*; S.-G. Park,* Hynix Semiconductor Inc., Korea, Korea, Republic of*; J.K. Lee,* Hynix Semiconductor Inc., Korea, S. Korea

Ta@sub 2@O@sub 5@ / PE-SiN MIM capacitors with high capacitance density of 4.7 fF/µm @super 2@ for mixed-signal / RF applications were originally integrated by adopting 120Å-thick-PE-SiN as a barrier layer between bottom electrode and 80-Å-thick MOCVD Ta@sub 2@O@sub 5@ layer. Inserting PE-SiN layer resulted in dramatic reduction of leakage current at -3.3 V from 8.0E-5 A/cm@super 2@ with only Ta@sub 2@O@sub 5@ film to 9.3E-8 A/cm@super 2@ with Ta@sub 2@O@sub 5@/PE-SiN layers. We attribute the huge reduction in leakage current for the laminated structure that the PE-SiN layer provides high barrier height as well as a physical diffusion barrier against oxygen into the bottom electrode. These laminated MIM capacitors also showed good linearities of capacitance with 302 ppm/V@super 2@, 125 ppm/V, and 30.7 ppm/°C as well as an excellent matching property with 0.79 % µm. Breakdown voltage of capacitor was about 6 MV/cm and the life time (time-to-breakdown) of Ta@sub 2@O@sub 5@/PE-SiN MIM capacitor at 3.7 V and 25°C was 198000 years. Quality factor of 55 and capacitance density of 5.08 fF/µm @super 2@ at 2.4GHz were obtained for 10X10 µm @super 2@ MIM capacitor.

DI-MoP5 The Physical and Electrical Characteristics of p@super+@-Polycrystalline-Si and Si@sub1-x@Ge@subx@(x=0.27)/High-k Gate Dielectric (AlN and Al@sub2@O@sub3@) Films*, **C. Lee**, J.Y. Park, C.H. Hwang, H.J. Kim,* Seoul National University, Korea

The polycrystalline (poly) Si@sub1-x@Ge@subx@(x=0.27) gate has been also investigated as a substitute of poly-Si gate, which seems not to be suitable for new high-k dielectrics and gives rise to troubles due to poly-depletion effect (PDE) and boron penetration. We investigated the compatibility between the poly-Si@sub0.73@Ge@sub0.27@ gate and high-k gate dielectrics in terms of the boron and germanium diffusion behaviors and electrical characteristics of stack structures, which were prepared with or without a capping or bottom AlN layer on high-k Al@sub2@O@sub3@ of MOS capacitors. The metal-oxide-semiconductor (MOS) capacitors characterized in this experiment include various high-k gate dielectric stacks such as p@super+@-poly-Si gate/ Al@sub2@O@sub3@/n-type Si, p@super+@-poly-Si@sub0.73@Ge@sub0.27@ gate/Al@sub2@O@sub3@, AlN-Al@sub2@O@sub3@, or AlN-Al@sub2@O@sub3@-AlN/n-type Si. High-k dielectrics like Al@sub2@O@sub3@ and AlN films were deposited on n-type Si (100) wafers with a resistivity of 4~8 @ohm@cm by atomic layer deposition (ALD) technique using Al(CH@sub3@)@sub3@, O@sub3@, and NH@sub3@ at 400°C after RCA SC1 and diluted HF cleaning. The physical thickness of the AlN films was controlled very thin (~ 0.5 nm). Post deposition annealing (PDA) of the samples was performed with rapid thermal annealing (RTA) at 800°C in N@sub2@ for 30 seconds. Post-metallization annealing (PMA) was performed at 400°C for 30 min under a 5% H@sub2@ + 95% N@sub2@ atmosphere. Capacitance equivalent thickness (CET) decreased by approximately 30 % for the p@super+@-poly-Si@sub0.73@Ge@sub0.27@ gate compared to the p@super+@-poly-Si gate with the Al@sub2@O@sub3@ films at the same physical thickness, which resulted from the improved PDE. Leakage current density of MOS capacitors with AlN barrier layers shows a lower value compared to that of the single Al@sub2@O@sub3@ film due to the enhanced boron blocking properties.

DI-MoP6 Structure Properties and Thermal Stability of Plasma Oxynitrided Hf and Zr Thin Films***, Yi-Sheng Lai****, L.-M. Chen, C.-H. Lu, J.S. Chen,* National Cheng Kung University, Taiwan

Thermal stability is a critical issue in replacing conventional SiO@sub 2@ gate dielectrics with high-@kappa@ materials. The interlayer (IL) growth as well as the interface reaction is of particularly concern in this respect. Growth of the low-dielectric-constant IL usually increases equivalent oxide thickness (EOT) of the high-@kappa@/IL structure, leading to the applicability in the downscaling of the electronic devices. Accordingly, engineering of the interface becomes a challenging issue in fabricating high-@kappa@ gate dielectrics. In this work, we study the characteristics of plasma oxynitrided Hf and Zr thin films. A 50-Å thick Zr or Hf metal film is first deposited on the Si surface and followed by plasma oxynitridation on these metal films in a mixture of N@sub 2@O+NH@sub 3@ ambient. Incorporation of O and N leads to the formation of ZrO@sub x@N@sub y@ and HfO@sub x@N@sub y@ films. The increased nitrogen content is found to increase the onset of the crystallization temperature in both ZrO@sub x@N@sub y@ and HfO@sub x@N@sub y@ films. Growth of the IL examined from the X-ray photoelectron spectroscopy is also dependent on the incorporated nitrogen content. The thermal stability related to the difference of nitrogen content between ZrO@sub x@N@sub y@ and HfO@sub x@N@sub y@ films is also addressed.

DI-MoP7 Valence Band Offsets and Interface Structure of Hf@sub X@si@sub 1-X@o@sub 2@ Films on Si(111) from Photoemission Spectroscopy***, L. Fleming****,* North Carolina State University*; M.D. Ulrich,* Army Research Office*; C. Hinkle, J.G. Hong,* North Carolina State University*; J.E. Rowe,* University of North Carolina*; G. Lucovsky,* North Carolina State University*; A.S.-Y. Chan, T.E. Madey,* Rutgers University

We have used synchrotron radiation to perform high resolution soft x-ray photoemission spectroscopy measurements on device-quality Si(111)/Hf@sub x@Si@sub 1-x@O@sub 2@ films. Our samples included both thick (~ 75 Å) and thin (~ 10 Å) silicate films. In addition, we grew SiO@sub 2@/HfO@sub 2@/SiO@sub 2@ layered films for interface studies. All samples were grown by remote plasma enhanced chemical vapor deposition at a temperature of 300 °C using hafnium tert-butoxide and silane in a helium carrier gas. After growth, thin film silicate samples were heated by rapid thermal annealing at 500 °C for 30 s, while the thick film silicates and layered structures were annealed at temperatures between 500 and 900 °C. Si 2p and Hf 4f core levels were studied along with valence band spectra using photon energies of 70, 100, 130, 150 and 170 eV. Core-level binding energies exhibit a linear dependence with alloy composition in the thick silicate films, and are expected to provide some information about the interfacial structure and relaxation behavior of the layered oxide films. We have used several photoemission methods for obtaining the band offset parameter as a function of the Hf/Si composition including edge extrapolation and core-level shift data. The linear edge approximation yields a valence band offset of ~ 2.9 ± 0.1 eV for an ultrathin film of HfSiO4. This value agrees with estimates of 3.0 - 3.1 eV based on unpublished tunneling data. Valence band offsets for other compositions will be presented based on data from thick oxide films.

DI-MoP8 Dry Etching of HfO@sub 2@ Films by Inductively Coupled Plasma***, S.-K. Yang****, H.-Y. Song, S.-G. Lee, B.-H. O, I.-H. Lee, C.-W. Kim,* Inha University, South Korea*; S.-G. Park,* Inha University, South Korea, Korea, Republic of

Not only deposition of high quality high-k dielectric layer but its dry etching is very important for fabrication of complete gate stack structure. In this study, 2000Å thick HfO@sub 2@ films are deposited on Si wafers for etching experiments by reactive sputtering and annealed in oxygen. Dry etching of HfO@sub 2@ is investigated in Cl@sub 2@, SF@sub 6@, HCl or Ar based ICP plasma. Etching characteristics are investigated in terms of RF powers, chamber pressures and gas compositions. It is found that physical sputtering effect enhances the formation of volatile hafnium halides. Single etching recipe is successfully used to pattern multiple layers of Pt/HfO@sub 2@/Si structure.

DI-MoP9 Structural and Optical Properties of Erbium-doped Ba@sub 0.7@Sr@sub 0.3@TiO@sub 3@ Thin Films***, S.Y. Kuo,*** National Science Council, Taiwan, R.O.C.*; W.F. Hsieh,* National Chiao Tung University, Taiwan

The Er-doped Ba@sub 0.7@Sr@sub 0.3@TiO@sub 3@ (BST:Er) thin films prepared by sol-gel technique have been investigated by means of x-ray diffraction (XRD), Raman, C-V, and photoluminescence (PL) measurements. While the sintering temperature is increased from 600°C to 700°C, the peaks of the XRD patterns become sharper and more intense, indicating better crystallinity and larger grain size. On the other hand, the crystallinity becomes worse as a result of phase separation and charge compensation mechanism when sintering temperature is above 700°C. We have shown that the addition of Er-dopant does not reduce the dielectric property of BST thin films in C-V measurement. Excitation-dependent PL studies indicate that these emission peaks do not shift with the change in excitation power, whele the integrated intensity increases exponentially with the increase in excitation power. Additionally, green emission intensities of the BST:Er films increase as the Er doping concentration increases from 1 to 3 mol%, and then quench due to the presence of clusters as doping concentration exceed 3 mol%. Besides, the improvement of the crystallinity of BST:Er films will result in the luminescence enhancement as well. These experimental results indicated that the BST:Er thin films might be a potential candidate for optoelectronics devices.

DI-MoP10 Comparison of Forming Gas Effects on the Ferroelectric Properties Between More-oriented and Less-oriented Pb(Zr@sub 0.53@Ti@sub 0.47@)O@sub 3@ Thin Films***, E.S. Lee****, H.W. Chung, S.H. Lim,* Yonsei University, Korea

More-oriented and less-oriented Pb(Zr@sub 0.53@Ti@sub 0.47@)O@sub 3@(PZT) thin films were deposited by pulsed laser deposition method on (Pb@sub 0.72@La@sub 0.28@)Ti@sub 0.93@O@sub 3@ buffer and Pt/Ti/SiO@sub 2@/Si substrate, respectively, which were observed by XRD patterns. These films were annealed in H@sub 2@-contained ambient for 30 minutes at the substrate temperature of 400 °C to evaluate the forming gas annealing effects. The comparative studies on the ferroelectric properties of these two films were carried out, which are shown that the degradation rate of the more-oriented film is lower than that of less-oriented film. These results have proven that well oriented structures can prohibit the diffusion of the hydrogen into the film.

DI-MoP11 Effect of Pb(Zr@sub 0.52@Ti@sub 0.48@)O@sub 3@ Buffer Layers on the Fatigue Resistance of Pb(Zr,Ti)O@sub 3@-Pb(Mn,W,Sb,Nb)O@sub 3@ Thin Films*, S.Y. Lee,* ***S.H. Lim****, E.S. Lee, H.W. Chung,* Yonsei University, Korea

The effect of a Pb(Zr@sub 0.52@Ti@sub 0.48@)O@sub 3@ (PZT) buffer layer on a perovskite Pb(Zr,Ti)O@sub 3@-Pb(Mn,W,Sb,Nb)O@sub 3@ (PMWSN) thin film deposited on a Pt/Ti/SiO@sub 2@/Si substrate was examined. The film having stoichiometric PMWSN composition was deposited directly on the Pt/Ti/SiO@sub 2@/Si substrate by pulsed laser deposition. While as-grown PZT-PMWSN thin films have poor fatigue resistance, PZT-PMWSN thin films with PZT buffer exhibit good fatigue resistance. The insertion of PZT buffer layer contributes to enhance the crystallinity of PZT-PMWSN and it can protect to diffuse the accumulated charges at the interfaces between electrodes and the films.

DI-MoP12 Comparison of Ferroelectric Properties Between PZT (Pb(Zr,Ti)O@sub 3@) -PMWSN (Pb(Mn,W,Sb,Nb)O@sub 3@) Thin Film and PZT Thin Film***, C.S. Jeon****, E.S. Lee, H.W. Chung, S.Y. Lee,* Yonsei University, Korea

Pb(Zr,Ti)OPb(Zr,Ti)O@sub 3@-Pb(Mn,W,Sb,Nb)O@sub 3@ (PZT-PMWSN) targets were fabricated using typical bulk ceramic processes. Thin films were deposited on Pt/Ti/SiO@sub 2@/Si substrate by pulsed laser deposition. Structural characteristics were measured by XRD (X-ray diffraction). Ferroelectric properties of thin films were investigated by P-E and C-V measurements to define hysteresis loops and dielectric constants. Results of PZT-PMWSN thin films were compared with those of PZT thin films. Leakage current of PZT-PMWSN thin film was higher than that of PZT film and crystallization was less oriented than that of PZT film. But P@sub r@ (remanant polarization) and dielectric constant showed higher values than those of PZT film.

Electronic Materials and Processing
Room Exhibit Hall B - Session EM-MoP

Poster Session

EM-MoP1 Oxidation of Epitaxial Al/Si(111) for Improved Josephson Tunnel Junctions*, **D.A. Hite**, R. McDermott, R.W. Simmonds, K.B. Cooper, M. Steffen, S. Oh, S. Nam, J.M. Martinis, D.P. Pappas,* NIST

One of the most promising candidates for a physical quantum bit (qubit) is the current biased Josephson junction. Quantized energy levels in the Josephson potential form the basis for the qubit and are manipulated by the application of currents at microwave frequencies. Recently, qubit spectroscopy (level spacing vs. dc bias current) has identified spurious resonances that have been shown to be a major source of qubit decoherence. Currently, all experimental evidence and modeling point to two-level fluctuators in the material system of the tunnel barrier as the origin of these spurious microwave resonances. In the present technology, tunnel junctions are grown as a trilayer by magnetron sputter deposition of Al with subsequent thermal oxidation for the tunnel barrier. In this talk, we will detail our efforts to identify and eliminate the spurious resonators by engineering epitaxial Josephson junctions with varying degrees of crystalline qualities and impurity concentrations. In particular, we will discuss the oxidation of ultra smooth Al films epitaxially grown on Si(111) as the base electrode of the tunnel junction. During each step in the Al/AlOx/Al trilayer growth, the structure has been investigated in situ by AES, AED and LEED. While tunnel junctions fabricated with these epitaxial base electrodes prove to be of non-uniform oxide thickness and too thin, I-V characteristics have shown a lowering of subgap currents by an order of magnitude. Transport measurements will be correlated with morphological structure for a number of devices fabricated with various degrees of crystalline quality.

EM-MoP2 Nickel Silicide Formation and Strain Relaxation of SiGe Layers during Rapid Thermal Annealing of Ni/cap-Si/Si0.83Ge0.17/Si(001) Structure*, **C.H. Jang**,* Sungkyunkwan University, South Korea*; Y.W. Kim,* Seoul National University, Korea*; M.R. Sardela Jr.,* University of Illinois at Urbana-Champaign*; Y.J. Song, K.-H. Shim,* Electronics and Telecommunications Research Institute, Korea*; N.-E. Lee,* Sungkyunkwan University, South Korea

NiSi or NiSi@sub 1-y@Ge@sub y@ has been intensively investigated for contact applications in CMOS devices utilizing strained Si or SiGe layers for better device performance. Recently, NiSi@sub 1-y@Ge@sub y@ layers formed from the direct reaction of Ni/SiGe structure showed a better thermal stability but a rough interface compared to NiSi on Si substrate. Therefore, NiSi/SiGe structure with improved interface flatness for a better control of the ultra-shallow depth of contacts needs to be investigated. In this study, the electrical and structural characteristics of nickel silicides formed on p-Si@sub 0.83@Ge@sub 0.17@/Si (001) using a sacrificial Si capping layer (cap-Si) and strain relaxation of SiGe layers during nickel silicidation were investigated. The phase formation of nickel silicide and interface quality between nickel silicide and the SiGe layer were measured by XRD (X-ray diffraction) and TEM (transmission electron microscopy), respectively. Sheet resistance of nickel silicide on p-Si@sub 0.83@Ge@sub 0.17@ /Si(001) substrate was investigated by four-point probe measurements. Chemical composition and depth profile of nickel silicide was examined by AES (auger electron spectroscopy). The surface roughness of nickel silicide films was measured using AFM (atomic force microscope) and surface morphology by FE-SEM (field-emission scanning electron microscopy). Strain relaxation behaviors of SiGe layers during Ni silicidation were investigated by high-resolution XRD and reciprocal space mapping (RSM) study. The results showed the formation of nickel monosilicide at 400~550°C and the sheet resistance values of 6.533 ~7.918 @ohm@/sq. But, increase in sheet resistance values above T@sub A@ @>=@600°C is attributed to the formation of high-resistivity silicide phase and surface roughening by agglomeration of nickel silicides. Detailed changes in lattice parameters and mismatch in the SiGe layers will be presented.

EM-MoP3 The Change of Microstructures in SiGe Film Grown on (001) Si Substrate using Solid Phase Epitaxy*, **S.G. Kim**,* ETRI, South Korea

SiGe films grown on Si substrate have a great interest for the application in high performance heterojunction bipolar transistors. In this system, study on the growth behavior and the microstructure is very important for the growth of defect-free SiGe film. In this work, we have investigated the growth behavior and the microstructure change of SiGe film on Si substrate grown by solid phase epitaxy (SPE) method. Amorphous Si1-xGex (x=0.2, x=0.35, x=0.5) films(~150nm) were deposited on (001) Si substrate by molecular beam epitaxy method and then crystallized (i.e SPE) at various anneal temperatures. These films were analyzed using glancing angle X-ray diffraction and transmission electron microscopy (TEM). For the Si0.8Ge0.2 sample annealed at 550â"f for 30 min, SiGe film was found to be amorphous. Single crystal SiGe film (~30 nm) with defects were formed in the sample annealed at 650â"f for 10 min, but very small amount of polycrystalline and amorphous SiGe layers still remained above the SiGe single crystalline layer. The preferred growth direction of polycrystalline SiGe layer was (111). For the Si0.8Ge0.2 film annealed at 750â"f for 10min, single crystalline SiGe layers was developed near SiGe/Si interface, and above the single crystalline layer, polycrystalline SiGe layer was formed with preferred growth direction of (220). For the Si1-xGex film with x>0.2, similar microstructure was formed but preferred growth direction changes with anneal temperature from (111) to (311) instead of (220).

EM-MoP4 Investigation of Thermal Stability of Strained Si on Relaxed SiGe Layer*, C.H. Jang, J.W. Lee, C.W. Yang,* Sungkyunkwan University, South Korea*; M.R. Sardela Jr.,* University of Illinois at Urbana-Champaign*; Y.J. Song, K.-H. Shim,* Electronics and Telecommunications Research Institute, Korea*; **N.-E. Lee**,* Sungkyunkwan University, South 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 enhanced channel mobility and compatibility with conventional Si CMOS processes. For the practical adoption of strained-Si channels into nano-CMOS technology, fabrication methods of strained-Si/relaxed SiGe/Si structures and their compatibility with post-thermal processes are to be obtained. In particular, stability of strained-Si channels on relaxed SiGe layers is of great concern because formation of misfit and threading dislocations and increase of surface roughness can occur during elevated temperature processing due to thermal-induced instability of strained-Si layers. In this study, we investigated thermal stability of strained-Si on relaxed SiGe layer at elevated RTA (rapid thermal annealing) temperatures. Strained-Si channel layers on the relaxed Si1-xGex(x=0.2) buffer layer were deposited by reduced-pressure chemical vapor deposition (RP-CVD). In order to investigate the thermal stability of fabricated strained-Si/relaxed-SiGe/Si(001), RTA treatments were carried out at the temperature range of 700~950°C in N@sub 2@ ambient for 60sec. Strain relaxation behaviors of strained-Si layer were investigated using Raman spectroscopy and reciprocal space mapping (RSM). Analyses of defect formation and structure of strained-Si were also performed by analytical transmission electron microscopy (AEM). And evolution of surface roughness and morphology upon RTA was measured using atomic force microscope (AFM) and field-emission scanning electron microscopy (FE-SEM). The combined results indicate that strained-Si is unstable due to strain relaxation leading to defect formation and increased surface roughness at the RTA temperature ï,³ 900 oC in the present experiments. Detailed results on strain relaxation behaviors of the strained-Si will be presented.

EM-MoP5 Application of IR Variable Angle Spectroscopic Ellipsometry to the Determination of Free Carrier Concentration in n@super ++@ Germanium*, **D.W. Thompson**, N.J. Ianno, K. Zhou,* University of Nebraska-Lincoln

Free carrier concentration profiles were determined by Fourier Transform Infrared (FTIR) variable angle spectroscopic ellipsometry in arsenic doped n@super ++@ germanium. This technique exploits carrier absorption in the mid-infrared range and combines the sensitivity of ellipsometry with a simple Drude free carrier absorption model to determine the carrier profile. The germanium was doped from an arseno silica spin-on source in an open tube furnace under a reducing atmosphere. Peak dopant concentrations were in excess of 10@super 19@/cm@super 3@ over depths greater than 10 @microns@ as determined by secondary ion mass spectrometry (SIMS). Shallower profiles were more effectively detected using ellipsometry. The optical modelling scheme approximated the depth profile of the carrier concentration using a large number of discrete layers. The effect of using different functional dependences such as Gaussian and error function was compared.

EM-MoP6 Study on the Enhancement of the Etch Selectivity of Photoresist for Next Generation Lithography*, **C.H. Shin**,* Samsung Electronics Co. Ltd., Korea, Republic of Korea*; J.Y. Yun, G.J. Min, C.J. Kang, H.K. Cho, J.-T. Moon,* Samsung Electronics Co. Ltd., Korea

As device feature size shrinks to sub 100nm, process applications using 193nm ArF lithography are being increased in the semiconductor industry. However, as the resolution of photoresist increases, carbon ratio and phenyl group in the resist structure decrease (Ohnish parameter increases), with the reduction of dry etch resistance. Moreover, as industry turns to the NGL such as F@sub 2@ and immersion ArF for sub-70nm patterning, limitations in the fabrication of patterning using NGL lie in both decreased physical thickness of photoresist below 2000Å and reduced hardness of materials. Dry etch resistances of immersion ArF and F@sub 2@ photoresist were evaluated in line and space pattern. Etching was performed in the commercially available dual frequency plasma using O@sub 2@, Ar, CF@sub 4@, CHF@sub 3@ and CH@sub 2@F@sub 2@ gas chemistries. It was found that dry etch resistances of NGL photoresist were weaker compared to the commercial ArF photoresist. Novel techniques forming a protective layer on photoresist will be discussed in this paper in order to improve dry etch resistance of new resist together with the enhancement of etch selectivity.

EM-MoP7 Inductively Coupled Plasma Etching of Nano-Sized Magnetic Tunnel Junction Stack for MRAM Fabrication*, S.W. Hwang*, *S.J. Jung, T.W. Kim, D.J. Ma,* Samsung Advanced Institute of Technology, South Korea

There is a strong interest in the development of plasma etching processes for magnetic multilayer structures of the type used in sensores, magnetic random access memories(MRAM). MRAM offers high storage density, fast access time, and infinite rewrite capability. Therefore, there is trend towards nano-size to increase bit storage density. The method for patterning the magnetic tunnel junction(MTJ) stacks that comprise the MRAM is ion milling, which has problems such as sidewall redeposition, etc. In conventional reactive ion etching, the MTJ stack do not form sufficiently volatile etch products to allow efficient pattern transfer. One alternative would be to increase the substrate temperature during etch process in order to increase the vapor pressure of the etch products. This method is not a good option, because of the limited thermal stability of MTJ stacks. In this study, magnetic tunnel junction(MTJ) stacks on Si/SiO@sub2@ were etched using inductively coupled Cl@sub2@-based plasma and the effects of Cl@sub2@-based gas mixtures on the formation of reactive byproducts affecting on MTJ stack etching were investigated. When Cl@sub2@-based gas mixtures were used with Ar or O@sub2@, due to very low vapor pressure of the etch products, thick etch products remaining on the etched MTJ stack could be observed. However, these etch products were easily removed during the etching, especially when BCl@sub3@, C@sub2@F@sub6@ were added to Cl@sub2@/Ar. These results are interpreted as the formations of more reactive products when BCl@sub3@, and C@sub2@F@sub6@ were added to Cl@sub2@/Ar. Therefore, the physical and chemical properties of the etch products formed by the specific gas mixture appear to be important in nano-sized etching of MTJ cell stacks.

EM-MoP8 Influence of Molybdenum on the Whisker Formation of Al Film*, C.F. Lo*, *D. Draper, P. McDonald, P. Gilman,* Praxair Electronics

This study was to understand if addition of Mo can minimize whisker formation of Al film. Four Al-Mo alloys with 5at%, 10at%, 15at% and 40at% Mo, respectively, plus one pure Al were deposited to glass substrates by physical vapor deposition. The as-deposited and 350C/1hour annealed films were characterized by the SEM-EDS and XRD. Many hillocks were observed on the as-deposited and annealed Al films, but no whisker was found. The as-deposited Al-5at% Mo film has a similar microstructure as that of the Al films. An enormous amount of whiskers with various shapes were formed after annealed. For the Al-10at%Mo and the other higher Mo content films, the hillocks were significantly reduced and no whisker was found. The XRD measurements showed that the Al and Al-10at% Mo films were (111) grain orientation dominant. The Al-5at% Mo, however, has the similar amount of (111) and (200) orientations. No grain orientation could be identified for the Al-15at%Mo and Al-40at% Mo films. Focusing on the whisker formation of the Al-5at% Mo film, a group of films annealed at 350C for 1 to 20 minutes were prepared. Increasing the holding time reduced the (111) oriented grains, while the (200) ones were not significantly changed. In addition, a new phase was formed after annealing. The results show that with at least 10at% addition of Mo, the hillock can be minimized and no whiskers will be generated. Addition of 5at% Mo, however, will generate whiskers by annealing at 350C. Formation of the whiskers on the annealed Al-5at% Mo was ascribed to the co-existence between the (111) and (200) oriented grains, which caused a higher internal stress as result of mismatch of the grain orientations. During annealing, to reduce the internal stress, the whiskers were generated.

EM-MoP9 Change of Structural and Electrical Properties due to Phase Transition of Ge@sub 2@Sb@sub 2@Te@sub 5@*, Y.K. Kim*, *S.A. Park, J.H. Beack, M.K. Noh, K.H. Jeong, E.J. Jeong, D.-H. Ko,* Yonsei University, Korea*; M.-H. Cho,* Korea Research Institute of Standards and Science, Korea

Ge @sub 2@Sb @sub 2@Te @sub 5@ ternary alloy film is used for phase-change nonvolatile memory device. This material shows electrical switching phenomena of resistance (~10 @super 6@ times) when phase transition occurs. In this research, we investigated the changes of structural and electrical properties after the phase of film transited from amorphous state to poly crystalline state. Phase transition of the alloy film grown by RF magnetron sputtering method was induced by post annealing treatment in N @sub 2@ ambient. XRD analysis showed that as-dep. film which was amorphous state crystallizes to NaCl fcc structure at 160~170 °C. As a result of DSC experiment, the effective activation energy for this crystallization is 2.5 ±0.11eV. Sheet resistance decreased from 10 @super 9@ to 10 @super 3@ @ohm@/sq. When it was annealed at 250 °C, phase transition from NaCl fcc structure to Hexagonal structure occurred. But not only hexagonal structure, other phases-Te and GeSb @sub 2@Te @sub 4@ hexagonal structures also appeared. This phase separation phenomenon also can be shown in SPEM(Scanning Photoemission Microscopy) data. In this phase, the sheet resistance decreased to 10 @super 2@ @ohm@/sq. AFM and XRR results show that while the crystallization occurs the surface roughening proceeds and thickness is decreased so that eventually the density increases. Hall measurement results indicate that resistance change is related to the change of hall concentration which is due to structure transition.

EM-MoP10 On the Surface Morphology of CdTe Thin Films Evaporated onto Rotating Substrates*, G.G. Rusu*, *M. Rusu,* Al.I. Cuza University, Romania

CdTe thin films were prepared by thermal evaporation under vacuum by quasi-closed volume technique onto unheated glass substrates. During the evaporation process, the substrates holder were periodically passed (by rotational moving) over the evaporating source. As result of step by step deposition, multi-layered films were obtained. Depending on the rotating speed (varied between 20 and 210 rpm) and source temperature the thickness of the individual layers ranged from 0.75 nm to 7.60 nm. The total film thickness, ranged between 320 and 510 nm. For samples deposited in various conditions, AFM investigations were performed and the average roughness (a-r) and the root mean square surface (rms) roughness were calculated. The obtained results revealed a strong dependence of film surface morphology on the source temperature and rotational speed. At lower temperature source (925 K), the surface roughness decreases (from 2.30 to 0.57 nm) with increase of rotational speed, v, while at greater source temperature (1165 K) the surface roughness increase (from 0.50 to 2.10 nm) with v. Also, at greater source temperature, the films present a tellurium excess. The heat treatment of the films determines the increase of surface roughness and the precipitation of tellurium excess as nanocrystallites embedded in CdTe films.

EM-MoP11 Future Super Conducting MeB@sub 2@ Materials*, I. Arvidsson*, *A. Pallas, K. Larsson,* Uppsala University, Sweden

Metal diborides (MeB@sub 2@) often have interesting thermal, mechanic and superconducting properties. MgB@sub 2@ was put into focus some years ago for its high transition temperature (39 K) in combination with its simple AlB@sub 2@-structure. The boron structure in MeB@sub 2@, with interesting similarities to graphite structures, is much dependent of the electron transfer from the nearby metal atoms. An electronic and structural comparison has here been performed for various planar and puckered transition metal borides using quantum mechanical calculations. In comparison to MgB@sub 2@ the transition metal diborides MoB@sub 2@, ZrB@sub 2@, RuB@sub 2@, and PdB@sub 2@ have been examined. The first two are planar with AlB@sub 2@ structure and the latter two have in experiments been shown to have a structure similar to puckered CaSi@sub 2@. The theoretical method used in the calculations is the density functional theory (DFT). Calculations were performed for each of the metal diborides as both planar AlB@sub 2@-structures and as puckered CaSi@sub 2@-structure. Extensive test calculations have been performed to ensure the accuracy of the model template and the calculation parameters. The results indicate that there are differences in stability for the planar and puckered structures. This variance in thermal stability was found to strongly correlate to differences in electron transfer between the metal atom and the boron skeleton.

EM-MoP12 Optical properties of Zn@sub1-x@Mn@subx@S epilayers by Spectroscopic Ellipsometry*, **D.-J. Kim**, S.-H. Eom, Y.-M. Yu, Y.D. Choi,* Mokwon University, Korea*; M.-Y. Yoon,* Joongbu University, Korea*; I.-H. Choi,* Chung-Ang University, Korea

II-VI compounds with transition metal Mn are generally referred to as diluted magnetic semiconductors (DMS), and they can be crystallized in the NaCl, zincblende and wurzite structure defined by the binary host crystal structure. ZnMnS is one of the widely studied systems among the DMS groups and is led to a wide range of technological applications as functional layers in electronic and optoelectronic devices, solar cells and sensors. Therefore, these materials have attracted much interest because of their various structural and optical properties. ZnMnS epilayers were grown on GaAs (100) by hot-wall epitaxy. The grown films had zincblende structure, which was confirmed from x-ray diffraction spectra. The Mn composition ratios of the epilayers were determined using the electron probe x-ray micro analyzer. The surface morphologies with Mn compositions were observed by atomic force microscopy. And a spectroscopic ellipsometry was used to know the optical properties by dielectric constants. The measured dielectric function spectra reveal distinct structures at energies of E@sub0@, E@sub0@+@delta@@sub0@, E@sub1@, E@sub1@+@delta@@sub1@, and E@sub2@ critical points (CPs). The complex refractive index n*=n+ik, the absorption coefficient @alpha@, and the normal incidence reflectivity R were deduced from dielectric constants @epsilon@@sub1@ and @epsilon@@sub2@. Also, a shifting and a broadening of the CPs can be observed. A new CP appears in the vicinity of 7.0 eV with the increasing Mn composition.

EM-MoP13 Effect of Mn Composition on Characterization of Zn@sub1-x@Mn@subx@S Epilayers*, **Y.-M. Yu**, D.-J. Kim, S.-H. Eom,* Mokwon University, Korea*; K.-S. Lee, T.-H. Kim,* Chungnam National University, Korea*; Y.D. Choi,* Mokwon University, Korea

ZnMnS is one of II-VI diluted magnetic semiconductors. The crystal structure of the bulk ZnMnS is cubic in the range of the Mn composition for x<0.1 and hexagonal for 0.1<x<0.6. And there is cubic NaCl type structure for x=1. ZnMnS epilayers were grown on the GaAs (100) substrates by hot-wall epitaxy. From the x-ray diffraction (XRD) spectra and the double crystal rocking curves (DCRC), the structural properties of ZnMnS epilayers were investigated. And Mn composition x was determined by electron probe x-ray micro analyzer (EPMA). The absorption and the temperature dependence of the photoluminescence (PL) were measured to study the optical properties of the epilayers. The relation between the Mn composition x determined by EPMA and the lattice constants by DCRC was found to be consistent with the Vegard law. From ZnMnS (200) and (400) XRD peaks and EPMA results, it was found that the stoichiometric ZnMnS epilayers with zincblende structure were grown on the (100) GaAs substrate in the wide range of x. The Mn composition dependence of PL peak energy at low temperature and the band gap energy at room temperature was investigated. The intra-Mn@super 2+@ transition at near 2.1 eV was strongly observed in the 10 K PL spectrum and the peak energy was constant with the increasing Mn composition x. And the temperature dependence of PL peak energy and intensity was also investigated. With the increasing temperature, the intra-Mn@super 2+@ transition energy red-shifts weakly up to 60 K and then blue-shifts. The absorption and PL spectra at 10 K were compared. It was found that PL peak near the energy band gap was related to the free exciton from the absorption measurements. From Raman measurement at the low temperature, ZnS-like LO phonon peak was observed, and with the increasing Mn composition x the red shift of ~6 cm@super -1@ was observed.

MEMS and NEMS
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Poster Session

MN-MoP1 Fabrication of PLT Thin Film Waveguides by Low Temperature Two-Step Pulsed Laser Deposition Processes*, **J.-S. Kao**,* National Science Council, Taiwan, Taiwan, ROC*; D.-R. Liu, C.-H. Tsai,* National Science Council, Taiwan*; I.-N. Lin,* Tamkang University, Taiwan

Lanthanum-modified lead titanate (PLT) thin films have attracted much attention in the application of integrated optical devices due to their high optical transparency and superior electro-optical (EO) properties. Optical signals propagation loss is the most important concern for these waveguide type devices. Because the optical absorption, scattering and leakage result from various waveguides structure defect, including PLT concentration proportion, grain boundary, surface roughness and waveguide structure, they will attenuate optical signals through the waveguide. The fabrication of PLT films have been well-developed by utilizing sputtering, chemical sol gel and excimer pulsed laser deposition (PLD) processes, whereas there is few study on the device application because of its difficulty on either wet or dry etching in microfabrication. In this study, the Pb@sub 1-x@La@sub x@TiO@sub 3@ (x = 0.28) thin films were synthesized at 150°C on MgO (100) substrates by frequency-quadrupled Nd:YAG pulsed laser (266 nm) deposition process with a defocused laser beam. Followed by 600°C post-annealing in oxygen atmosphere, the PLT planar thin film waveguides with smooth surface, high transparency and texture were produced. These characteristics were revealed by atomic force microscopy, UV/VIS/NIR spectrophotometry, and x-ray diffractometry examination. Propagation loss of the planar waveguides were measured by a prism coupler. A PLT 28 planar waveguide with a low propagation loss less than 1dB/cm was successfully prepared. Two-step PLD and lift-off processes were introduced to fabricate the ridge type channel waveguides. The light propagated properties of these waveguides were also examined by using IR (1550 nm) capture of scattered light method.

MN-MoP2 Three-Terminal Nano-Manipulator Fabrication by Focused-Ion-Beam Chemical-Vapor-Deposition*, **M. Kawamori**, R. Kometani, S. Matsui,* University of Hyogo, CREST-JST, Japan

We have demonstrated that the highly functional nano-mechanical devices with three-dimensional structure can be fabricated by using focused-ion-beam chemical-vapor-deposition (FIB-CVD). So far, we reported the nano-manipulator using electrostatic repulsion between 2 terminals with the same polarity by FIB-CVD. However, there was one disadvantage which was a high operation voltage over 300 V. To reduce an operation voltage, we have proposed a 3 terminal nano-manipulator which is composed of two external-terminals and one center-terminal. The polarity of external-terminals are different from that of a center-terminal. The principle of movement is as follows. When positive and negative voltages are applied on 2 external-terminals arranged outside and a center-terminal arranged inside, the external terminals are attracted to a center-terminal by a electrical attractive force. Features of three-terminal nano-manipulator are as follows. (1) Since the tips of two outside terminals are homo-polar, both insulator and conductive materials can be manipulated. (2) As the structure is 3 terminals, a control accuracy of operation is improved. (3) Since an electrostatic attraction force is applied, it can operate on a lower voltage than that of 2 terminal nano-manipulator. The experimental result indicates that an operation voltage of 3 terminal nano-manipulator was 60 voltage, which was a lower voltage than that of 2 terminal nano-manipulator.

MN-MoP3 Enhancement of Piezoelectric Properties of Silver Doped Pb(Zr,Ti)O@sub3@-Pb(Mn,Wn,Sb,Nb)O@sub3@ Thin Films*, **H.W. Chung**, S.H. Lim, E.S. Lee,* Yonsei University, Korea*; S.Y. Lee,* Yonsei university, Korea

The dielectric and piezoelectric properties of silver doped Pb(Zr,Ti)O@sub3@-Pb(Mn,W,Sb,Nb)O@sub3@ thin film deposited on a Pt/Ti/SiO@sub2@/Si substrate by pulsed laser deposition has been investigated depending on silver contents. By varying the contents of silver from 0 ~ 1 mol.%, the effect of silver doping on PZT-PMWSN thin film was systematically observed. No reaction between silver and PZT is observed in X-ray diffraction analysis. As increasing silver contents, it is observed that the relative dielectric constant increased because of effective electric field in the dielectric phase.

MN-MoP4 Electron Transport in Nanomechanical Devices*, P. Datskos, **N.V. Lavrik**,* Oak Ridge National Laboratory

New phenomena can be observed in electronic nanosystems because of quantum confinement, the resonant electronic structure associated with this confinement and due to the discreet nature of electric charge. More recently, we have explored Focused Ion Beam (FIB)-induced growth in order create vertical pillar-like nanomechanical structures using direct-write FIB-assisted growth. These nanomechanical resonators have resonance frequencies in the range of 1 to 30 MHz. We have created Si QPC structures using an FIB milling approach that consists of a suspended microbridge (about 2000 nm long) with a narrow (20-40 nm) constriction in the middle of the microbridge. Mechanical actuation of the structure was found to cause significant modulation of stress in the nanobridge region and, in turn, changes in the Si bandgap. We found that mechanical deformations act as a gating mechanism for the electron transfer through the nanoscale constriction. Our preliminary results confirmed modulation of the electron current through the suspended nanorestriction upon its actuation with a modulated diode laser. The fabricated structures suffered from poor mechanical stability and loss of mechanical integrity during our experiments. Furthermore, mechanical and photonic effects of laser actuation still need to be delineated. We will discuss our findings and address potential problems associated with the designs and approaches.

MN-MoP5 Deep Quartz and Silicon Etching in Newly Proposed ICCP Plasma*, **Y. Morikawa**, T. Koidesawa, T. Hayashi, K. Suu, M. Ishikawa,* ULVAC, Inc., Japan

We have developed a new etching system for MEMS application. This System provides combined plasma of inductive coupled plasma (ICP or NLD) and a kind of capacitive coupled plasma (CCP), which is named as ICCP (Inductive coupled and capacitive coupled plasma). Using this system, deep silicon etching is capable even if fluorocarbon gas and SF@sub 6@ are not fed in the etching process. So this system is very friendly in view of GWP. SiO@sub 2@ etching is carried out in the NLD@footnote 1,2@ Plasma, which is generated by forming the magnetic neutral loop in the ICP plasma. The NLD plasma has a higher electron density with lower electron temperature at low pressure below 1 Pa, compared with that of ICP. The selectivity of SiO@sub 2@ to PR is improved to obtain more than 50 by tuning the contribution of inductive and capacitive plasma discharge. Silicon deep etching was carried out with the SiO@sub 2@ mask in the ICCP plasma, in which the electrodes were timely modulated for etching and deposition at a high-pressure region above 2 Pa. The selectivity of 300 or more was obtained for SiO@sub 2@ mask. The etch rate was about 15um/min when SF@sub 6@ was fed and about 5um/min when Ar/F@sub 2@ mixed gas was fed. Typically, the depth of 80 um or more with the trench width of 35 um was anisotropically etched at the etch rate of 10 um/min by the electrode modulation method in the ICCP plasma, in which cleaning step was not necessitated. Thus, even if the global warming gases were not used, deep Si etching was achieved. This is the most striking feature of the ICCP etching system. @FootnoteText@ 1)W. Chen et al, J.Vac. Sci. Technol. A19(6) (2001) 2936 2)Y. Morikawa et al., J.Vac. Sci. Technol. B21(4) (2003) 1344 .

MN-MoP6 Wafer Scale Replication of a Micro-well Array Assay Chip*, **M.W. Lee**, S.-B. Jo, K.-C. Lee, K.J. Lim,* Inha University, South Korea*; J.K. Suh,* LGLS, South Korea*; B.-H. O,* Inha University, South Korea

Technological issues regarding microfabrication of a micro-well array chip are presented. Microfabrication processes have been widely used to make a micro-mold using micromachining processes based on the semiconductor fabrication processes. Its intermediate product is a wafer mold. It can be used as a parent of other molds, like a Ni electroplated mold. Or, the intermediate wafer can be used as a mold directly for a polymer replica. In this study, polymer replication processes using an intermediate wafer, a Ni electroplated mold, and a wafer mold coated with anti-adhesive layer are performed and the corresponding characteristics are compared. Target device is a polymer based micro-well array assay chip. The Si wafer was patterned conventionally and etched by using ICP. The Ni mold showed good performances for replicating the polymer assay chip. As it was not adequate to use the intermediate as-etched Si wafer as a mold for the polymer replication due to the adhesion problem, Teflon-like film was coated as an anti-adhesive layer on top of it. Replication performance of the film coated wafer mold was good enough to replace the Ni mold. Multiple replications were carried using the coated wafer without stiction problems, enough to be used as a mold in a mass replication process.

MN-MoP7 Development of a Disposable Microchip with Capillary Electrophoresis and Integrated Three-Terminal Electrochemical Detection*, **J.H. Kim**, M.C. Moon, Y.S. Kim,* Myongji University, Korea

We have developed a microsystem with capillary electrophoresis (CE) and electrochemical detector (ECD). The microfabricated CE-ECD systems are adequate for a disposable type and the characteristics are optimized for an application to the electrochemical detection. The system was realized with polydimethylsiloxane(PDMS)-glass chip and indium tin oxide (ITO) electrode. The injection and separation channels (80 m wide 40 m deep) were produced by moulding a PDMS against a micro fabricated master with relatively simple and inexpensive methods. ITO electrode was fabricated by patterning the ITO film deposited on a fusion glass. A capillary electrophoresis and a three-electrode electrochemical detector were fabricated on the same chip. Unlike analogous CE/ECD devices previously reported, no external electrodes were required. The surface of PDMS layer and ITO-coated glass layer was treated with UV-Ozone to improve bonding strength and to enhance the effect of electroosmotic flow. The running buffer was prepared by 10 mM 2-(N-morpholino)ethanesulfonic acid (MES) titrated to pH 6.5 using 0.1 N NaOH. The testing analytes are consisted of 1 mM catechol and 1 mM dopamine. Separation of catechol and dopamine was performed using an electric field strength of 60 V/cm after applying an injection electric field of 50 V/cm. The ECD circuit was adjusted to maintain a potential of +600 mV DC between the working and reference electrodes. The electrochemical detection circuit could mostly decouple the interference of a separation electric field. The root-mean-square noise level was ~10 pA on a signal 10 nA in 10 mM MES. The limit of detection for dopamine was ~0.5ï�-M The disposable CE/ECD system showed similar results with the previously reported expensive system in the limit of detection and peak skew. When we are using disposable microchips, it is possible to avoid polishing electrode and reconditioning.

MN-MoP8 Dissipative Processes in Single-Paddle and Double-Paddle Nanomechanical Silicon Resonators*, **J. Li**, S. Evoy,* University of Pennsylvania

Resonant nanomechanical devices represent powerful platforms for the detection of physical, chemical, and biological processes. However, mechanical quality factor is known to decrease at small dimensions, and the origins of the dominant dissipative mechanisms in resonators of such scales remain misunderstood. We report a study of energy dissipation of nanomechanical resonators through a set of differing devices designed to help isolate and identify dominant dissipative mechanisms. The resonators are fabricated by the nanomachining of silicon-on oxide layers, and characterized by a laser interferometry technique Geometries include double-clamped and single-clamped cantilevers, as well as single-paddle and double-paddle torsional resonators. We will first report on the linear and non-linear dynamics of these devices. Resonant frequencies and the low to mid MHz range and qualities reaching Q = 15 000 are observed in single clamped and doubly clamped structures of width w = 2 um, length from 5 um to 40 um, and thicknesses of t = 150 nm to 400 nm. For the double paddle torsional devices with symmetric geometry, 4 modes of motion are observed which are ascribed to the in-phase/anti-phase flexural, and in-phase/ anti-phase torsional modes of the paddles. For 150 nm thick devices, the resonant frequencies are f0 = 1.9 MHz, 3.55 MHz, 4.10 MHz, and 8.67 MHz respectively. For double paddle design with asymmetric geometry, two flexural modes are observed at 1.19 and 2.86 MHz, respectively. Onset of non-linear behavior is observed under large excitation amplitudes in several of the devices. We will also report a study of the impact of aging, process induced-damage, controlled ion beam induced damage, as well as post-processing annealing on the performance of these resonators. Such results will allow the isolation of the impact of such issues on devices of various designs, dimensions, and geometries.

MN-MoP9 Plasma-Free Etch Chemistry to Realize Defect-free GaAs Micromechanical Resonator Structures@footnote 1@*, **S.W. Kang**, S.B. Shim, J.H. Kong, K.R. Char, Y.D. Park,* Seoul National University, Korea

We report on the fabrication of GaAs micromechanical resonator structures utilizing plasma-free etch chemistry, by utilizing latticed-matched MOCVD grown GaAs(0.5 µm)/In@sub 0.5@Ga@sub0.5@P(0.5 µm) alloy system patterned by selective wet-etch chemistries. GaAs (100) cap layer was defined with photoresists and patterned in a citric acid/H@sub 2@O@sub 2@ solution, resulting in near vertical side-wall profiles. After GaAs cap patterning and resist removal, HCl solutions of varying concentrations were investigated for selectivity of InGaP over GaAs for various conditions: temperature, agitation, and differing crystallographic directions. For 12 M HCl solution, vertical etch-rate was found to be ~3 µm/min under agitation. Lateral etch of InGaP layer between GaAs layers starts with initial etch fronts of vee, mixed, and dovetail observed by cross-sectional SEM with predominance of dovetail etch front for lateral etch direction 45° from the cleave direction. The lateral etch rate at 20°C for 12 M HCl solution was highly directional dependent with GaAs cap edge patterned parallel to the cleave direction [011] to be nearly zero and edge 45° from the cleave direction to be ~1 µm/min, similar behavior as observed by Cich et al.@footnote 2@ For increasing dilution of HCl, the etch rate, especially lateral etch rate, was drastically reduced, with no observable lateral etch for 1:4 HCl:H@sub 2@O. For all HCl solutions, high selectivity of InGaP over GaAs was observed. Micromechanical GaAs resonator structures with aspect ratios as high as 30 was realized by simply drying in a flow of dry N@sub 2@ gas. Along with the investigation of etch chemistry, expected benefits of plasma-free fabrication of GaAs-based NEMS resonators will be presented. @FootnoteText@ @footnote 1@ This work is partly supported by KOSEF and Samsung Electronics Endowment through CSCMR and by KIST Vision 21 Project.@footnote 2@ M.J. Cich et al., Appl. Phys. Lett. 82, 651 (2003).

MN-MoP11 Determination of Young's Modulus for Silicon Membrane in Cryogenic Micropump using Laser Michaelson Interferometry*, **Y. Zhao**, B. Li, X. Zhang,* Boston University

In micro satellites, lots of dedicate instrumentations were compacted in a limited room for demonstration of new concepts. The ambient temperature would rise if heat generated could not be well dissipated, which will ruin many heat sensitive devices, such like infrared camera. As a solution, a two phase loop using micro pump was used to keep a narrow cryogenic range. This micropump depends on elastic deformation of silicon membrane to transfer cryogen. The mechanical properties of the membrane, especially elastic modulus, are thus critical in heat balance analysis. However, conventional tensile experiment was not practicable for non bulk material and in cryogenic environment. In this paper, we report the work using laser Michaelson interferometer for Young's modulus measurement of thin membrane in cryogenic environment. Square membranes were fabricated on SOI wafers. The membrane deflection was achieved using laser Michaelson interferometer. Actuating with differential pressure of compressive gas, the dependency of deflection upon temperature was achieved. Given the actuating pressure and membrane geometry, Young's modulus of the membrane was consequently obtained. It was found Young's modulus increases with decreasing temperature, indicating a much stiffer material in cryogenic environment. A calibration was further carried out utilizing longitudinal wave propagating along the membrane thickness. The membrane was locally vibrated using 1064 nm Nd:YAG laser. The generated longitudinal wave was examined at the same point by laser Michaelson interferometer. Young's modulus derived from the propagating velocity corresponds with previous deflection measurement. It provides a feasible way to determine membrane stiffness in cryogenic environment, which is not limited to single material membrane, but also good for any composite membranes, like silicon membrane deposited with oxide film, which is not readily practicable using other current approaches.

MN-MoP12 Process Integration for Through-Silicon Vias*, S. Burkett, L. Schaper, **Z. Rahman**, G. Vangara, S. Spiesshofer, S. Polamreddy,* University of Arkansas

Development of an integrated process flow for the fabrication of Cu filled vias in silicon will be described. The formation of a through-silicon via (TSV) enables three-dimensional (3-D) interconnects for chip-stacking applications that will be especially important for integrating heterogeneous devices. A strong motivation for 3-D interconnects is the much reduced time delay that will be observed by connecting chips at the via or interconnect level rather than through conventional metallic wiring. The formation of a TSV involves many processing steps with the major areas including: via formation; deposition of via insulation, barrier, and Cu seed films; Cu electroplating for via-fill; wafer thinning; and backside processing. The via diameter is 4-8 @micron@, via depth is 15-20 @micron@, and a 20 @micron@ pitch is used in this study. Vias formed at these dimensions will result in a high interconnect density. A primary challenge to implementation of 3-D stacking is the process integration involved in TSV technology. A major requirement is that the techniques in the integrated process flow are chemically, mechanically, and thermally compatible. Vias are formed by both conventional reactive ion etching (RIE) and by the Bosch process using deep RIE (DRIE). These processes will be compared. The via profile that is obtained determines the step coverage that will be achieved in the subsequent thin film deposition steps. SiO@sub2@ deposited by PECVD forms the via lining; sputtered TaN and Cu provide barrier and seed films, respectively. A fountain Cu reverse pulse electroplating method is used to fully fill the vias. A carrier wafer is required at this point for handling thin wafers. Wafer bonding of this carrier wafer involves a lamination process and wafer thinning involves mechanical grinding, chemical spray etching, and a blanket etch to open the vias. Each step will be described in the process flow with the considerations discussed for successful process integration.

MN-MoP13 Processing and Characterization of MEMS Thermal Switches for Emittance Control*, **S.L. Firebaugh**, M.A. Beasley,* United States Naval Academy*; R. Osiander, A.C. Keeney, R.L. Edwards,* Johns Hopkins University

The trend towards smaller satellites requires a new type of thermal control. Current thermal control systems do not scale well with miniaturization. An alternative is to coat the satellite with an active "skin," formed by many microelectromechanical devices, that can control the emissivity of the satellite surface. Previous work has explored the use of microscale louvers and shutter arrays @footnote 1@. An alternative technique is to insert a variable thermal conductivity layer between the satellite and an emissive outer surface @footnote 2@. Our approach uses a MEMS switch to implement the variable thermal conductivity layer. This system relies on gold membranes, coated with an emissive upper layer and suspended above the device substrate on polymer posts. The application of a voltage pulls the devices into contact with the substrate, resulting in conduction of heat from the substrate to the outer layer, where the energy can be emitted as light. Prior work has described the initial prototype and test results for this design @footnote 3@, which verified the electrostatic model for the device. These prototype devices, however, were not optimized for thermal performance and did not include the high-emissivity layer which is crucial to device operation. This poster will discuss the implementation of the second generation design of the device, which includes design modifications and the development of a high-emissivity coating layer. @FootnoteText@ @footnote 1@ R. Osiander et al., "Microelectromechanical Devices for Satellite Thermal Control," to appear in IEEE Sensors J., August 2004. @footnote 2@ W. Biter et al. "Electrostatic Radiator for Spacecraft Temperature Control," Space Technology and Applications International Forum (STAIF 2004), pp. 96-102. @footnote 3@ M. A. Beasley et al., "MEMS Thermal Switch for Spacecraft Thermal Control," SPIE Photonics West Conference, San Jose, California, Jan 13-29, 2004.

Plasma Science and Technology
Room Exhibit Hall B - Session PS-MoP
Poster Session

PS-MoP1 Photoresist Stripping after Low-k Dielectric Layer Pattering Using Axial Magnetic Field Assisted Reactive Ion Etching*, **H.-Y. Song**, C.-W. Kim,* Inha University, South Korea*; J.-K. Yang, C.-W. Lee,* PSK Tech Inc., South Korea*; S.-G. Park,* Inha University, South Korea, Korea, Republic of*; B.-H. O, S.-G. Lee, E.-H. Lee, D.H. Park, G.-J. Kim,* Inha University, South Korea

Effects of axial magnetic field added to the conventional Reactive Ion Etcher(RIE) are studied in terms of plasma characteristics and it is applied to photoresist strip process of dual damascene Cu/low k multi-level interconnection technology. Photoresist remaining on low k dielectric layer should be removed by anisotropic plasma in order to keep vertical profile of low k layers. The magnitude and direction of axial magnetic field can be controlled by the current to a pair of Helmholtz coils. Compared to the conventional RIE, It is found that strip rate is increased by more than 25 % from 1.0 µmm/min and its uniformity is also improved over 300 mm wafers. The effects of axial magnetic field in RIE are also investigated in terms of the selectivity of photoresist over SiOC-H dielectric films and the plasma damage of low k dielectric layers in O@sub 2@/N@sub 2@ plasma. The chemical structures of the low-k SiOC-H film are measured by FTIR spectrometer and the presence of the axial magnetic field is found to suppress any chemical changes of the films while providing wider process window.

PS-MoP2 Etching Characteristics of Organic Polymers by Plasma Beam Irradiation*, **K. Kurihara**,* Toshiba Corp., Japan*; A. Egami, M. Nakamura,* Association of Super-Advanced Electronics Technologies, Japan

Copper interconnection and low-k dielectric interlayer are promising technologies for reducing the RC delay of LSI devices. Organic polymers such as SiLK and GX-3 are one of the candidates of the low dielectric materials. The chemical formulas of these materials have not been clearly opened to the public due to company secrets. It is, therefore, difficult to forecast the characteristics of etching behavior based on the experience. It is important to investigate the relation between the etching behavior and the chemical formulas of organic material for understanding of the fundamental etching mechanisms. In this study, we prepared three kinds of organic films whose compositions were clearly identified. They were methacrylate polymer films, which were polytbutylmethacrylate (PtBuMA), polycyclohexylmethacrylate (PCHMA) and polybenzylmethacrylate (PBMA). The chemical formulas of these films have the same main chain with a different side chain. We investigated the etching characteristics such as etching yield (EY) using a plasma beam irradiation apparatus which can control the plasma parameters precisely. The etch yields of PCHMA and PBMA increased with increase in the ion energy and were saturated over around 330 eV. The etch yield of PtBuMA did not depend on the ion energy above 130 eV. These etch yield behaviors look like the other organic materials such as GX-3 and this can be the notable etching characteristics of organic films. Furthermore we measured desorbed products during nitrogen plasma etching by using a time-of-flight technique. Major desorbed products were HCN and C@sub 2@N@sub 2@ for all organic films we used, and very small amount of C@sub 6@H@sub5@ which is a part of the side chain was also observed in the case of PBMA etching. We will discuss the etching characteristics of organic material based on surface analysis using an in-situ X-ray photoelectron spectroscopy and an energy distribution of the desorbed products. This work was funded by NEDO.

PS-MoP3 Effects of Ar Plasma on DVS-BCB Monomer Used for Low-k Film Deposition*, **T. Wakai**, T. Shirafuji, K. Tachibana,* Kyoto University, Japan

Divinly siloxane bis-benzocyclobutene (DVS-BCB) is an attractive monomer because practical low-k films can be prepared by plasma polymerization of this monomer.@footnote 1@ Recently, its dissociation reaction due to electron impact has been investigated with mass spectroscopy, and fragmentation pattern in the plasma has been discussed by Kinoshita et al.@footnote 2@ However, the DVS-BCB plasma contains excited noble carrier gas and ions, and its effects are not investigated yet. Therefore, we have investigated effects of Ar plasma treatment on DVS-BCB monomer on c-Si with in situ FT-IR reflection absorption spectroscopy. ICP (13.56MHz, 200W) was used for the treatment at room temperature. Duration of the treatment was varied, and temporal change of the spectra was monitored. It has revealed that major reaction due to Ar plasma treatment is opening of benzocyclobutene ring in the monomer. Various bias voltage on the sample was examined during the treatment, which revealed that the ring opening occur even without bias voltage although a few ten eV of plasma potential exists. This means that there are important reaction paths in addition to electron impact dissociation, which can be used for triggering polymerization of DVS-BCB without high energy electrons. Details will be discussed including effects of emission from Ar plasma. This work was supported by NEDO. @FootnoteText@ [1] J. Kawahara et al, Plasma Sources Sci. Technol. 12, S80-S88 (2003). [2] K. Kinoshita et al, Proc. 25th Int. Symp. Dry Process, Nov.13-14, 2003, Tokyo (2003) No.3-01.

PS-MoP4 A New Plasma Source for Destruction of Organic Material in the Post Chamber Hardware, and Implications for Process Endpoint Detection for Specific Low-k Applications.*, **A.K. Srivastava**, P. Sakthivel,* Axcelis Technologies, Inc.*; T.J. Buckley,* Formerly, Axcelis Technologies, Inc.*; A.F. Becknell,* Axcelis Technologies, Inc.

The high temperature ash of photoresist in the presence of certain oxygen-sensitive low k materials requires a plasma discharge devoid of conventional oxidizing agents. In such cases, the chemistries active on the wafer do not entirely destroy the long chain organic polymers that make up the resist. Instead, some of the photoresist is re-deposited on the chamber walls, as well as in the hardware downstream of the wafer. Specifically, parts of the vacuum system comprising the throttle valve, foreline valve and pump lines get coated with organic material, which then have to be manually cleaned during frequent maintenance periods. This leads to significant down time for the ash tool. Due to this oxidizer-free process, there are few emissions in the visible region of the spectrum from reactions at the wafer surface, which makes conventional optical emission based end-point schemes mostly unusable. A compact plasma system has been developed that creates an intense radio frequency (RF) discharge in the exhaust line below the process chamber. Using a secondary inlet for oxidizer agents, the plasma system combusts all incoming organic material before it has a chance to redeposit on the post chamber hardware. Data will be shown on the observed destruction efficiency. Additionally, analysis of the plasma using a residual gas analyzer (RGA), as well as an optical spectrograph to obtain crucial information on the reaction chemistries will be presented. RGA data from diffusion tests show that no oxidizing agent from the downstream inlet makes its way upstream into the chamber where it could potentially harm the low-k material on the wafer. Finally, successful oxidation of the organic material in the plasma source gives rise to optical signals downstream of the chamber that can be used very effectively to extract endpoint for resist removal from the wafer surface.

PS-MoP5 RF-plasma Functionalization of Large Quantity of Carbon Nanotubes: XPS and AFM Analysis of O2 and CF4 Treatments*, **A. Felten**, C. Bittencourt,* LISE, Belgium*; S. Cuenot, R. Daussin, C. Bailly,* Universite Catholique de Louvain, Belgium*; J.-J. Pireaux,* LISE, Belgium

Polymer based electromagnetic screening materials are highly requested nowadays. The fabrication of this material can be achieved by mixing conductive additives to a polymer matrix. CNT are promising ones due to their unique properties. However the formation of homogeneous composite with as grown nanotubes presents a technological difficulty, due to a low compatibility between macromolecules and CNT. To overcome this problem a modification of nanotubes surface by changing their chemical composition was proved to be efficient. There are several ways to modify the CNT surfaces (chemical, plasma@footnote 1@@footnote 2@, fluorination,...). In this work we use inductive RF plasma to functionalize the CNT surface. The nanotubes are Multiwalled prepared by CVD (Nanocyl) and arc discharge (Mercorp). The influence of different plasma conditions (type of gas, power, treatment time, pressure, position of the sample in the discharge) on the functionalization of the CNT was analyzed by XPS. The obtained results show that the concentration of the functional groups bonding at the nanotube surface increased with the treatment time and the plasma power. Concerning the treatment by O2 plasma, the presence of hydroxyl and carboxyl groups has been confirmed by XPS analysis. Depending on the CF4 plasma conditions, it is possible to have either a functionalization of the CNT or a polymerisation of the monomer on the CNT surface. The treatment was scaled up to produce up to 2 grams of nanotubes at once by using magnetic stirring of the powder.An important step of this work was to define the optimal plasma conditions for which the concentration of the fixed functional groups was highest without destruct the nanotube surface. In this way, different plasma treatments were tested on the nanotubes and their surfaces were systematically characterized by atomic force microscopy (AFM).This work is supported by a grant from Region wallone, RW-ENABLE. @FootnoteText@ @footnote 1@H. Bubert et al., Diamond and Related Materials, Vol 12, 3-7, 811-815 (2003)@footnote 2@N. O. V. Plank et al., Applied physics letters, Vol 83, 12, 2426-2428 (2003).

PS-MoP6 Suppression of ArF Photoresist Deformation in Inductively Coupled Plasma (ICP)*, K.J. Lim, **S.-B. Jo**, K.-C. Lee,* INHA University, South Korea*; K.-Y. Jung,* CNI, South Korea*; S.-G. Park,* INHA University, South Korea, Korea, Republic of*; B.-H. O,* INHA University, South Korea

The ArF photoresist, which can be exposed at 193 nm wavelengths, has been applied in semiconductor manufacturing for a 0.1µm feature size and beyond. Recently reported results show that ArF photoresist is much weaker and thinner than KrF (248 nm) photoresist. It will be a challenge in plasma etch process to maintain the integrity of ArF photoresist, leading to be free of resist deformation during critical etch process such as Si@sub3@N@sub4@ hardmask opening. In this paper, plasma etch resistance and morphological changes of ArF photoresist in various plasma etching environments was checked. To determine the main etch parameter causing deformation of ArF photoresist, etching parameters in Inductively Coupled Plasma (ICP) source was varied and compared the results. We present alternative etch techniques consists of a triple sequence of protective layer coating, polymer / photoresist trimming and final etch step. The effect of fluorocarbon layer formation on selectivity and etch profile will be discussed.

PS-MoP7 Experimental Characterization of an Inductively-Coupled Acetylene/Hydrogen Plasma for Carbon Nanofibers Synthesis*, Y.Y. Lin,* National Tsing Hua University, Taiwan*; K.C. Leou,* National Tsing Hua University, Taiwan, ROC*; H.H. Wei, M.T. Wei, **C. Lin**, C.H. Tsai,* National Tsing Hua University, Taiwan

A plasma enhanced chemical vapor deposition process was employed to synthesiz carbon nanofibers on silicon or glass substrates patterened with Ni catalystic films. The plasma was generated by an inductive coil driven by 13.56 MHz RF power with acetylen and hydrogen gas mixtures. The substrates were placed on a temperature controlled staged which was also powered by 13.56 RF voltages. At gas pressure 15-25 mTorr and substrate temperature (surface) 500-600°C, isolated and vertically-aligned carbon nanofibers have been successfully synthesized. This paper reports experimental investigation of plasma properties characterized by optical emission spectroscopy of spectra line intensities of various species such as hydrogen, C@sub 2@ and CH, as well as RF properties at the biased substrate stage measured by RF impedance meter. Measurement results reveal that line intensity of C@sub 2@ increases with acetylene/hydrogen ratio. On the other hand, hydrogen atom density which was estimated by optical actinometry measurements(using Ar as the tracer gas) decreases accordingly. As a consequence, there was more @alpha@-C contents in the nanofibers as verified by both SEM imagies and micro-Ramman measurements. The ion current(or flux) incident on the substrate surface was estimated by the ratio of the RF power over RF voltage amplitudes as measured by the impedance meter. The ion current increased with ICP source power but changed little when the bias power was varied, as expected. The RF voltage amplitude, which is rougly proportional to ion energy, decreased as ICP power was increased. This is because plasma density increases with source power but the bias power is fixed.

PS-MoP8 In-Situ FTIR Characterization of Gas Phase Chemistry in Continuous and Pulsed Inductively Coupled 1,3-Butadiene Discharges in a Gec Cell, Cross-Correlated Against Ex-Situ ATR Surface Analysis*, **A.K. Jindal,*** The University of Texas at Dallas*; A.J. Prengler,* NEC*; J.R. Frautschi,* Western Life Sciences*; L.J. Overzet, M.J. Goeckner,* The University of Texas at Dallas

Gas-phase chemistry of 1,3-Butadiene plasmas and resulting deposited film chemistries are examined. In-situ Fourier Transform Infrared Spectroscopic (FTIR) diagnostics are used to characterize the chemistry at 50 mTorr pressure in continuous and pulsed regimes of the discharge, in an inductively coupled gaseous electronics conference cell. The continuous discharge was examined using a designed experiment with pressure, power, and gas flow being the free parameters. The pulsed discharge was examined at duty cycles ranging from 87 to 3 percent, all acquired at 50 mTorr, 8 sccm, and 60 W (during plasma "on" phase). When the plasma was pulsed with a 50 percent duty, approximately 10 percent of the polymer was broken apart. This increased to approximately 20 percent for the continuous discharge. Ex-situ Attenuated Total Reflectance (ATR) diagnostics are used to study the surface chemistry resulting from plasma deposition of Butadiene on bare silicon substrates under both continuous and pulsed regimes of the discharge, restricted to the same conditions presented above. Surface analysis in the pulsed modes was performed for each individual duty cycle, along with analysis of film grown using combined cycles. FTIR data is cross-correlated against the ATR data to better understand the interactions between plasma induced gas phase and surface chemistry. This work is supported in part by grants from NSF/DOE, CTS-0078669 and NSF, CTS-0079783.

PS-MoP9 Impact of Plasma Polymerization on Cd Bias and Ler*, **S.K. kim,*** Cypress Semiconductor, usa

CD bias and LER are the most critical factors to enable sub-90nm technology contact hole formation in terms of good Rs and barrier deposition. As pattern density increases, ARC (Anti-Reflective-Coating) layer is essential together with 193nm resist to print good contact holes. It, however, drives plasma contact etch much more challenging than before because ARC material is similar to PR(Photo Resist) and during the ARC plasma etch PR degradation is inevitable. In addition, oxide etch chemistry is evolving to create more carbon rich polymers for 193nm resist selectivity and is getting O2 gas dependant to control the amount of the polymer, which caused LER worse. In this study, impact of plasma polymerization during the plasma oxide etching on CD bias/LER was evaluated. Polymerization can be dominated by etching gas combination. Adding Freon 134(C2H2F4) into conventional ARCE chemistry such as CF4/CHF3 and oxide etch(C4F6/O2) enables to modulate CD bias/LER. Local non-uniformity of oxygen atoms in the contact hole is the root cause of LER. Etching sequence, adding dry CLN step at the end of oxide etch step is also play an important role on CD bias/LER as well. Furthermore, Impact of process parameters such as CF4/CHF3 ratio and etching time will be discussed.

PS-MoP10 Deformation of ArF Photoresist and Silicon Nitride Etching using Dual Frequency Superimposed (DFS) rf Capacitive Coupled Plasma*, **D.H. Kim,** S.H. Cho, J.G. Lee, N.-E. Lee,* Sungkyunkwan University, South 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 unpatterend ArF photoresists by varying the process parameters such as HF(13.56, 27.12, and 60 MHz)/LF(2 MHz) power ratio, pressure and etch chemistry (CHF@sub3@/CF@sub4@/CH@sub2@F@sub2@/Ar/O@sub2@/N@sub2 @). Characterization of surface chemical change was performed by X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared spectroscopy (FT-IR). Surface morphological changes also investigated by scanning electron microscopy (SEM) and atomic force microscopy (AFM). Also, morphological changes of surface and line edges in ArF PR, SiN etch rate, selectivity over PR during etching of ArF PR/BARC/SiN structures were investigated. The results indicated an increased deformation by increasing the low frequency power and flow rate of Ar and O@sub2@. Effects of process parameters on the etch results will be discussed in detail.

PS-MoP11 Si@sub x@O@sub y@F@sub y@ Passivation Layer in the Silicon Deep Etching Cryogenic Process*, **X.M. Mellhaoui,** R.D. Dussart, T.T. Tillocher,* ***P.L. Lefaucheux****, P.R. Ranson,* GREMI - Orléans University, France

Silicon etching is perfomed by a cryogenic SF@sub 6@/O@sub 2@ plasma process. This process allows to obtain a high aspect ratio (depth/width > 10) and a high anisotropy. The plasma is created in an Inductively Coupled Plasma reactor (Alcatel 601E). The silicon wafer is clamped on a electrostatic chuck cooled with liquid nitrogen and controlled in temperature with thermal resistances. A study of passivation mechanisms is necessary to perfectly control this process and to optimize the trench profiles. The passivating layer is a mixture of Si, F, O (Si@sub x@O@sub y@F@sub z@). Previous XPS experiments have shown that the passivation layer is removed during the increase of temperature. When destroyed, this layer can be rebuilt with a plasma mixture of SiF@sub 4@ and O@sub 2@. This particular experiment was made and has revealed that the presence of sulphur is not necessary to build an efficient passivation layer. In new experimental ICP reactor was equipped with a spectroscopic ellipsometer. This new diagnostic allowed to characterize the kinetic of passivation layer growing in the cryoetching process, and it desorption when the wafer is warmed. Mass spectrometry experiments were also carried to analyze the desorbed species These new results will be presented at the conference.

PS-MoP12 High Aspect Ratio Contact Hole Etching in C@sub 4@/F@sub 6@/O@sub 2@/Ar/CH@sub 2@F@sub 2@ and c-C@sub 4@/F@sub 8@/O@sub 2@/Ar/CH@sub 2@F@sub 2@ Plasmas*, H.-K. Ryu,* LG Chem, Ltd., Korea*;* ***C.B. Shin,*** Ajou University, Korea*; Y.-W. Kim,* Hynix Semiconductor, Inc., Korea*; C.-K. Kim,* Ajou University, Korea

A high aspect ratio contact hole etching of dielectrics (e.g., SiO@sub 2@) is one of the key processes in developing the next generation ultra large scale integrated devices because of the rapid shrinkage of the design rule to the nanometer level. To meet the several requirements for a high aspect ratio contact hole etching, a high etch selectivity to mask (e.g., photo resist) is practically required to maintain the critical dimension (CD) of the small-size contact hole. Also, bowing-free structures are needed for the etched profiles. Perfluorocarbons (PFCs) such as c-C@sub 4@F@sub 8@ are widely used as etchant gases for contact hole etching. These PFCs, however, are considered to be problematic from an environmental point of view because of their long atmospheric lifetimes and high global warming potentials (GWP). Several classes of environmentally benign chemistries have been examined as alternatives to PFCs and unsaturated fluorocarbons (UFCs) are one of the attractive candidates due to their shorter atmospheric lifetimes and lower GWP. In this study, we reports on an etching of a SiO@sub 2@ contact hole with a diameter of 0.17 µm and an aspect ratio of 15 using C@sub 4@F@sub 6@/O@sub 2@/Ar and C@sub 4@F@sub 6@/O@sub 2@/Ar/CH@sub 2@F@sub 2@ plasmas (UFC-containing plasmas). It was shown that the addition of CH@sub 2@F@sub 2@ gas made the CD of the contact hole to be maintained, reduced the degree of bowing, and enhanced the etch selectivity to photo resist during a high aspect ratio contact hole etching in a C@sub 4@F@sub 6@/O@sub 2@/Ar plasma. A SiO@sub 2@ contact hole etching in a c-C@sub 4@F@sub 8@/O@sub 2@/Ar/CH@sub 2@F@sub 2@ plasma (PFC-containing plasma) was also conducted to compare the etch profiles and contact resistances obtained in the two different gas discharges: C@sub 4@F@sub 6@/O@sub 2@/Ar/CH@sub 2@F@sub 2@ and c-C@sub 4@F@sub 8@/O@sub 2@/Ar/CH@sub 2@F@sub 2@ plasmas.

PS-MoP13 Investigation on the Plasma Parameters and the Properties of the Reactively Sputtered Titanium Oxynitride Thin Films*, **A. Karuppasamy,** A. Subrahmanyam,* Indian Institute of Technology Madras, India

The titanium oxynitride thin films were prepared by reactive dc magnetron sputtering of metallic titanium using a gas mixture of argon, oxygen, and nitrogen. The Argon and nitrogen flow rates were kept constant while the oxygen flow rate was varied .The target was sputtered with a constant current density of 90 Am @super-2@. The films were deposited on quartz and glass substrates, kept at a constant temperature of 573K. The in situ plasma discharge diagnostics were done by optical emission spectroscopy(OES)and Langmuir probe.The emission signal was detected by a miniature fiber optic spectrometer (Ocean Optics SD 2000) coupled with a quartz fiber in the spectral region from 350 nm to 850 nm. Emission lines of different species of titanium, nitrogen and oxygen were analyzed. The plasma parameters like the plasma potential, electron temperatures, plasma density and the ion energy distribution function (IEDF) were measured using Langmuir probe. The crystallographic structure and composition were examined by X-ray diffraction (XRD) and RBS.The temperature dependent electrical conductivity measurements in the range 10 K to 300 K shows an increase in the activation energy with increase in the oxygen content of the films. The index of refraction, extinction coefficient and thickness of the films were measured using a phase modulated spectroscopic ellipsometer in the energy range 1.65 - 3.1 eV. The transparent films were analyzed with Sellmeier dispersion relation while the semi-transparent films with Cauchy polynomial function. With increase in the oxygen flow rate, a sharp increase in the refractive index is observed. The optical transmittance spectra of the films were measured in the energy range 0.56 to 5.61 eV.The carrier concentration and mobility were estimated by low temperature(10 K) Hall measurements.Work function of the films were measured by contact potential method using the kelvin probe.The plasma conditions required for a high quality film will be discussed.

PS-MoP14 Anomalous Ionization of Copper Atoms in Argon-Based Sputtering Plasmas*, **H. Kadota**, K. Nakamura,* Chubu University, Japan*; N. Nafarizal, K. Sasaki,* Nagoya University, Japan*; M. Kobayashi,* ANELVA, Japan

Plasma-enhanced metal sputter deposition has been widely used for formation of seed and/or barrier layers of high aspect ratio contact holes in ULSI semiconductor devices. In this process, sputtered metal atoms are ionized during flight in Ar plasma, and the metal ions can arrive at the bottom of the hole since the metal ions are accelerated in the sheath around the wafer in the direction perpendicular to the substrate. This paper reports on ionization characteristics of sputtered copper atoms in Ar plasmas, especially for ionization fraction of the copper atoms as well as ion density ratio of copper to argon. An inductively-coupled argon plasma is produced in a stainless steel vessel by supplying 13.56 MHz RF powers with a loop bare copper antenna. A blocking capacitor is inserted in series at each end of the antenna conductor, consequently a negative self-bias voltage appears during the operation at the antenna. Therefore, copper atoms are injected into the plasma because of physical antenna sputtering. The ion density ratio [Cu@super +@]/[Ar@super +@] is obtained by combining mass spectroscopic measurements and Langmuir probe measurements, whereas the copper ionization fraction is measured with a biased crystal micro balance. The ion density ratio increases with the Ar pressure, and reaches ~30 at ~100 mTorr. The ionization fraction also increases with the Ar pressure and approximately reaches ~100% at the same pressure. This means that copper plasma is likely to be produced even in the argon discharge. These characteristics are independent to the discharge power, suggesting an ionization mechanism of the copper atoms except for electron impact.

PS-MoP15 Ionization Processes of Metal Atoms in High-Pressure dc Magnetron Sputtering Discharges*, **N. Nafarizal**,* Nagoya University, Japan*; K. Shibagaki,* Suzuka National College of Technology, Japan*; N. Takada,* Nagoya University, Japan*; K. Nakamura,* Chubu University, Japan*; M. Kobayashi,* ANELVA Corporation, Japan*; K. Sasaki,* Nagoya University, Japan

Ionized physical vapor deposition (IPVD) is a key technology in the formation of seed and/or barrier layers on the surfaces of trenches and holes with high aspect ratios. In IPVD, metal atoms sputtered from the target are ionized in the gas-phase, and metal ions are accelerated toward the biased wafer by the sheath electric field. To optimize this technique, it is necessary to know ionization processes of metal atoms. In the present work, we measured the density distributions of Ti and Ti@super +@ in dc magnetron discharges by laser-induced fluorescence imaging spectroscopy. We observed significant production of Ti@super +@ in the gas phase in high-pressure (@>=@100 mTorr) discharges. The distribution of the Ti@super +@ density had a peak at a distance of 5-6 cm from the target surface. Namely, the production of Ti@super +@ was obtained in dark plasma with a low electron temperature, and was not obtained in bright region near the target with a high electron temperature, indicating that electron impact ionization of Ti is not the production process of Ti@super +@. As another possible candidate of the production process of Ti@super +@, we investigated Penning ionization (collision between Ti and Ar@super M@) by measuring the density distribution of Ar at a metastable state (Ar@super M@). In addition, we estimated the density ratio between Ti@super +@ and Ar@super +@ from the total plasma density measured using a Langmuir probe. The result suggests that Ti@super +@ is the dominant ion in the down flow region of the high-pressure discharge.

PS-MoP16 Plasma Chemistry of a Nb/Ar/O@sub 2@ Magnetron Discharge*, **S. Mráz**, M. Wuttig, J.M. Schneider,* RWTH Aachen, Germany

We have investigated the plasma chemistry of a DC reactive magnetron discharge with a mass energy analyser. We have studied the effect of the oxygen partial pressure on the positive and negative ion populations of the discharge. The current supplied to the magnetron and the total pressure were kept constant throughout the experiments at 900 mA and 0.8 Pa, respectively. The plasma chemistry is strongly affected by the oxygen partial pressure. As the oxygen partial pressure is increased the formation of oxygen based positive and negative ions is observed. Furthermore, we present evidence for the oxygen partial pressure dependent presence of NbO based clusters, both positively and negatively charged. As the oxygen partial pressure is increased the NbO based clusters become the dominating Nb based ionic species in the plasma. These findings are of relevance for the chemical composition and structure evolution of thin NbO@sub x@ films.

PS-MoP17 Dry Etching of (Pb,Sr)TiO@sub 3@ Thin Films Using Inductively Coupled Plasma*, **C.I. Kim**, K.T. Kim, G.H. Kim,* Chungang University, Korea*; T.H. Kim,* YeoJoo Institute of Technology, Korea*; C.I. Lee,* Ansan College of Technology, Korea

Recently, ferroelectric thin films have received great attention for the application to high density memory devices. Among the various ferroelectric films, the BST thin film was noticed as the most promising material due to its high dielectric constant and paraelectricity at normal operating temperature. Although BST possesses a satisfactorily high dielectric constant, 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. Strontium titanate (SrTiO@sub 3@) is one of the few titanates which is cubic at room temperature. But, the dielectric constant is lower than BST. The addition of lead into strontium titanate makes its dielectric constant(1377) higher and the temperature of crystallization lower. Therefore, (Pb,Sr)TiO@sub 3@ (PST) thin film can be a promising material due to its high dielectric constant and paraelectricity at normal operating temperature. However, there is no report on the characteristics and mechanism of PST thin films during etching process. In this study, inductively coupled plasma etching system was used for etching PST because of its high plasma density, low process pressure and easy control bias power. The etching characteristics of PST thin films were investigated in terms of etch rates and selectivity as a function of gas mixing ratio, rf power, dc bias voltage and chamber pressure. The BCl@sub 3@/Cl@sub 2@/Ar plasmas were characterized by optical emission spectroscopy (OES), quadruple mass spectrometry (QMS) and Langmuir probe analysis. The chemical states on the etched surface were investigated with x-ray photoelectron spectroscopy (XPS) and secondary ion mass spectrometry (SIMS). Scanning electron microscopy (SEM) was used to investigate the etching profile.

PS-MoP18 Irregular Pattern Deformation in Etching of High Aspect Ratio Contact Holes*, **S.-I. Cho**, S.-Y. Son, Y.-J. Kim, M.-C. Kim, K.-K. Chi, C.-J. Kang, J.-T. Moon,* Samsung Electronics Co. LTD, South Korea

During the high aspect ratio etching process, the transferred pattern may be distorted by the deflection of ion trajectories due to the local charge build-up and nonuniform polymer deposition. The integrity of devices increases, high aspect ratio structures are required to meet the device architecture. Top-down shapes of the etched profiles are observed at various depths of contact holes with high aspect ratio. The top-down shapes are distorted and become irregular as the depth becomes deeper than the aspect ratio of 10. The degree of the pattern deformation is monitored at various process conditions using the contact holes with the aspect ratio of 17. The degree of the pattern deformation is changed with the process parameters, such as C/F ratio, residence time, bias energy, and frequency. We also investigate the correlation of the deformation with the radical species, bias energy, plasma density, and bias frequency by analyzing optical emission spectroscopy (OES), plasma potential, and auger electron spectroscopy (AES). The result of OES shows that the etched pattern becomes more severely distorted when the larger CF2 radicals exist in the gas phase. The profile deformation is not only controlled by polymer species but also by ion energy. The pattern distortion becomes worse by lowering ion energy. Based on results, irregular pattern transfer in high aspect ratio contact holes is caused by nonuniform polymer deposition and the deflection of ion trajectory due to the local charge build-up.

PS-MoP19 Etching Profile of (Ba,Sr)TiO@sub 3@ Thin Films in a BCl@sub 3@/Cl@sub 2@/Ar Inductively Coupled Plasma*, C.I. Kim, K.T. Kim,* ***G.H. Kim,*** Chungang University, Korea

(Ba@sub 1-x@,Sr@sub x@)TiO@sub 3@ (BST) thin film attracts a great interest as a new dielectric material in capacitors for the next generation ultra-large scale integrated dynamic random access memories (ULSI DRAMs), such as giga bit DRAM in the wide range of research institutes to semiconductor industries because of its large dielectric constant, low leakage current and low dielectric loss. In order to realize the higher integration, it is important to minimize the dimension of storage capacitors, simplify the memory cell structure and maintain sufficient accumulated electric charge within a smaller capacitor. Although BST thin films are excellent capacitor dielectric materials for DRAMs, there are several problems such as fine pattern transfer and no plasma induced-damage etc. In order to solve these problems, the etch behavior of BST with BCl@sub 3@/Cl@sub 2@/Ar gas mixtures is performed with inductively coupled plasma (ICP). In this study, inductively coupled plasma etching system was used for BST etching because of its high plasma density, low process pressure and easy control bias power. The etching characteristics of BST thin films were investigated in terms of etch rates and selectivity as a function of Cl@sub 2@/Ar and additive BCl@sub 3@ into Cl@sub 2@/Ar, rf power, dc bias voltage and chamber pressure. The Cl@sub 2@/Ar and additive BCl@sub 3@ into Cl@sub 2@/Ar plasmas were characterized by optical emission spectroscopy (OES), Langmuir probe analysis and quadruple mass spectrometry (QMS). In order to minimize the pattern transfer difference between a dense cell pattern and isolated pattern, we investigated the effects of process parameters (rf power, dc bias, process pressure and residence time) in Cl@sub 2@-based ICP etching. Scanning electron microscopy (SEM) was used to investigate the etching profile.

PS-MoP20 Characteristics of Neutral Beam Generated by 3-grid Low Angle Forward Reflected Neutral Beam System and its Etching Properties*,* ***D.H. Lee,*** *B.J. Park,* Sungkyunkwan University, South Korea*; G.Y. Yeom,* Sungkyunkwan University, South Korea, Korea

Plasma etching is widely used for the fabrication of deep submicron silicon based integrated circuits. However, plasma etching has a serious disadvantage due to the energetic charged particles such as positive ions and photons generated in the plasma which causes radiation damage resulting in physical defect, increased gate oxide breakdown, charging, etc. To avoid these charge-related and physical impact-related damages, several low-damage processes have been proposed. One possible alternative to avoid these problems is to use low energy neutral beam. In fact, many studies have been conducted previously and currently being conducted to generate parallel and low energy neutral beams and to etch materials vertically without having electrical charging and physical damage. In our study, to extract the parallel neutrals from the plasma, a neutralizing reflector having less than 5 degree sloped to the extracted ions was used which called low angle forward reflected neutral beam. In this study, the characteristics of a neutral beam and the etch characteristics of Si and SiO2 for SF6 gas have been studied using a low-angle forward-reflected neutral (LAFRN) beam system. In other to obtain higher neutral flux and lower beam energy, a 3-grid system was used to the neutral beam source and the neutral beam energy and flux was investigated using a quadrupole mass spectrometer.

PS-MoP21 Plasma Etching of Pyrex Glass by Inductively Coupled Plasma for Fabrication of Microfluidic Channel*,* ***J.H. Park,*** *N.-E. Lee,* Sungkyunkwan University, South Korea*; J.S. Park, H.D. Park,* Korea Electronics Technology Institute, South Korea

Among many micromachining technologies of glass for microfluidic channel fabrication, DRIE (deep reactive ion etching) has been becoming increasingly attractive because of the trend towards micrometer-scale and nanometer-scale pattern in the glass or quartz. However, low etch rate of glass during plasma etch has limited the usefulness of plasma etch in the fabrication of high aspect ratio structure of glass @footnote1-3@. In this study, DRIE of pyrex glass was carried out using SF @sub 6@-based gas chemistry in a commercial 8â? inductively coupled plasma (ICP) reactor (TCP 9100, Lam Research Corp.). The glass substrate used in this experiment was pyrex glass with the thickness of 700 µm and 1cmï,´1cm squared-shape. As a etch hard-mask, Ni was electroplated into patterned SU-8 photoresist mask with the line and spacing pattern of 12-15µm on Cu /Cr /glass structure. In case of using SF @sub 6@ only, edge profiles of glass showed under-cutting below the Ni hard mask due to chemical etching and trenching or cusping at the bottom of etched channel occurred. Etch rate of @<=@0.75µm/min was obtained. On the other hand, in case of using SF @sub 6@/Ar chemistry, profile improvement without under-cutting and trenching phenomena was observed compared to the case of SF @sub 6@ chemistry but etch rate was slightly decreased. Etch rate of @<=@0.54µm/min was obtained. Ar addition was effective in the removal of etch residues by high-flux Ar ion bombardment leading to improved profile and removal of bottom trenching. XPS results indicate that sputtering etching helps remove nonvolatile by-products such as AlF@sub3@, NaF, and BF. In case of SF @sub 6@ /C @sub 4@F@sub 8@/Ar chemistry, etch characteristics of pyrex glass were similar to those of SF @sub 6@ and SF @sub 6@ /Ar chemistries but glass etch rate was slightly increased. Optimized process showed the following performance: angle profile: >88°, and glass etch rate: 0.8µm/min.

PS-MoP22 Etching Characteristics of Al-doped ZnO Thin Films in ICP Etcher*,* ***S.W. Na,*** *M.H Shin, Y.M. Chung, J.G. Han, J.-H. Boo, N.-E. Lee,* Sungkyunkwan University, South Korea

Recently, the greatly increasing use of transparent conducting oxide (TCO) films such as indium tin oxide (ITO) for flat panel displays has promoted the development of inexpensive TCO materials including Al-doped ZnO (AZO). AZO films have high electrical conductivities as well as high optical transparencies. From the manufacturing viewpoint, TCO films should be easily etched in order to fabricate fine electrodes. Therefore, dry etch characteristics of ZnO and Al-doped ZnO films need to be investigated. In this study, etching characteristics of AZO thin films using inductively coupled plasma (ICP) etcher. AZO thin films with thickness of 300~400nm and different Al doping concentrations were prepared on wafer substrates by RF magnetron sputtering and photolithographic patterning of a positive photoresist mask (AZ7220) was followed. An rf power of 13.56MHz was applied to the top electrode coil to induce ICP. Bottom electrode power of 13.56MHz was applied to the substrate holder to induce self-bias voltage to the wafer. Plasma etching of AZO thin films was investigated by varying gas mixing ratio of Cl@sub2@/(Cl@sub2@+Ar) and CH@sub4@/(CH@sub4@+Cl@sub2@+Ar) chemistries, top electrode power, and bottom electrode power. Etch rate and profiles on different weight percent of AZO thin films were measured by the scanning electron microscopy (SEM). In order to understand the etching mechanism, optical emission spectroscopy (OES) and X-ray photoelectron spectroscopy (XPS) are used to investigate the chemical states of the etched surface with various gas mixing ratios. The etch rate was increased with increasing rf bottom power and top electrode power and the etch rate of >= 200 nm/min was achieved. From the various measurements, it was found that the addition of Cl@sub2@ and CH@sub4@ gases plays an important role in determining the etch arte. Etching characteristics of AZO films with different Al doping concentrations will be discussed in detail.

PS-MoP23 Effect of BCl3 Addition on Etching Characteristics of TaN in BCl3/Cl2/Ar Inductively Coupled Plasma*,* ***M.H Shin,*** *S.W. Na, N.-E. Lee,* Sungkyunkwan University, South Korea*; J.H. Ahn,* Hanyang University, South Korea

Patterning of absorbers is a crucial step in the manufacturing of EUVL (Extreme ultra-violet lithography) masks due to the stringent CD and reflectance requirements. So, patterning characteristics of new absorber materials for EUVL masks have to be evaluated [1]. Tantalum nitride (TaN) is one of the candidates for absorber layers in the mask used for the next generation EUVL and X-ray lithography because of the relative ease of patterning and its durability in cleaning processes. In this work, etching characteristics of 500-nm-thick TaN layers were investigated in a modified 8 inch commercial ICP (inductively coupled plasma) etcher having a 3.5 turn spiral copper coil on the top of chamber separated by a 1-cm-thick quartz window. RF powers of 13.56MHz were applied to the top electrode coil and the substrate holder to induce ICP and self-bias voltage to the wafer, respectively. In order to investigate the effect of BCl@sub 3@ addition to Ar/Cl@sub 2@ chemistry on the TaN etch characteristics, TaN etch rates were measured by changing the added BCl@sub3@ flow rate and the bottom electrode power while the Cl@sub 2@ and Ar gas flows are fixed at 80sccm and 20sccm, respectively. To understand the role of BCl@sub 3@ gas in BCl@sub 3@/Cl@sub 2@/Ar ICP etching, the relative change in the densities of Cl and Ar radicals and the chemical binding states of etched TaN surfaces were measured by optical spectroscopy (OES) and X-ray photoelectron spectroscopy (XPS), respectively. The results showed the relative density of the Cl radicals was higher in the BCl@sub 3@/Cl@sub 2@/Ar chemistry than in Cl@sub 2@/Ar chemistry at the same total gas flow rate. The effects of BCl@sub 3@ addition to Cl@sub 2@/Ar chemistry on the etch characteristics of TaN (etch rate, selectivity over SiO@sub 2@ buffer layer, etc) will be discussed in detail. [1] F. Letzkus, J

Butschke, M. Irmscher, F. M. Kamn, C. Koepernik, J. Mathuni, J. Rau, G. Ruhl: Microelectronic Engineering 2004.

PS-MoP24 High-density Plasma in Low-pressure will Cast a Bright Foresight in a 45 nm Node Etching Process*, Y. Morikawa, **T. Hayashi**, K. Suu, M. Ishikawa,* ULVAC, Inc., Japan

For the next-generation lithography, whose target dimensions are below the 100 nm realm, ArF lithography is considered to be a promising technique. However, an ArF resist has poor etching resistance, which brings on low mask selectivity and results in striation or pitting by resist degradation. This is a serious problem in a future device fabrication. We have studied etching characteristics of organic materials in view of pressure dependence and relations of etching species. Obtained results suggest organic materials are very reactive with atomic hydrogen, oxygen, halogen and other molecular radicals, and therefore, high density plasma in low pressure below 1 Pa is very useful to achieve anisotropic etching of organic films and porous dielectric materials with ArF resist mask without striation. Organic materials including ArF resist may react with radicals, so chemical / physical properties of the organic films may change and resulting degradation may occur under the energetic particle irradiation in the etching plasma. An important issue in the porous low-k etching process is the film damage(ref.1) (degradation of the etched sidewall). If the thick sidewall protective film is formed, this damage may be suppressed. However, it is necessitated that a thin protective film is formed on the sidewall in the finely patterned holes and lines below 100 nm. Nitrogen additive plasma may answer this problem. Under a certain etching condition, it was deduced that the protective thin film formed in the nitrogen additive plasma was composed by some kinds of fluorinated acrylonitrile polymer. 1) Y. Morikawa, N. Mizutani, M. Ozawa, T. Hayashi, W. Chen, and T. Uchida, J. Vac. Sci. Technol., B 21 (2003) 1334.

PS-MoP25 Study on Effects of Ion Irradiation on Plasma Anisotropic Cu CVD using a Triode Discharge*, **K. Takenaka**, T. Kaji, K. Koga, M. Shiratani, Y. Watanabe,* Kyushu University, Japan

Plasma anisotropic CVD method can realize bottom-up filling of Cu in a trench without sidewall deposition. @footnote 1,2@ This method is promising for Cu metallization in ULSI, since it has a potential to fill extremely narrow trenches and holes with a high aspect ratio. In order to reveal the anisotropic deposition mechanism, we have studied the deposition profile on a Si substrate with trenches using a triode discharge, for which a grounded mesh is placed at 10 mm above the substrate to control flux of ions impinging on the substrate. Without ion irradiation, nothing is deposited on the top, bottom and sidewall. With irradiation of ions of a low energy below 12 eV, the deposition rate on the top is 2 nm/min; while that on the sidewall increases with a trench width W from 0 nm/min for W @<=@ 1500 nm to 0.25 nm/min for W = 3300 nm, and the deposition rate on the bottom increases with W from 0 nm/min for W @<=@ 700 nm to 0.9 nm/min for W = 3300 nm. These results suggest the following three items; 1) ion irradiation is necessary for the deposition, 2) low energy ions are hard to reach the bottom of a narrow trench, 3) a fraction of low energy ions impinge on the sidewall of a wide trench. The items of 2) and 3) indicate that a width and an aspect ratio of trench have an influence on kinetic energy and flux of ions reaching bottom and sidewall. Based on the results, effects of ion irradiation on the plasma anisotropic CVD will be discussed in the presentation. @FootnoteText@ @footnote 1@ K. Takenaka, et al., Mater. Sci. Semicond. Proc. 5 (2003) 301.@footnote 2@ K. Takenaka, et al., J. Vac. Sci. Technol. A22(4) (2004) in press.

PS-MoP26 Deep Silicon Etch and In-Situ Passivation of Silicon Mold*, **S.-B. Jo**, S.-G. Lee, E.-H. Lee,* INHA University, South Korea*; S.-G. Park,* INHA University, South Korea, Korea, Republic of*; B.-H. O,* INHA University, South Korea

Silicon mold is attractive for polymer embossing applications, since the properties of silicon and micro-machining process have been highly characterized through the integrated circuit fabrication. In this article, we present modified Bosch process to obtain high aspect ratio silicon mold with conventional Inductively Coupled Plasma (ICP), without the need of expensive Bosch process systems. In modified Bosch process scheme, silicon etch / sidewall passivation time is much longer than commercialized Bosch process systems and process transition time was introduced between silicon etch and sidewall passivation. Etch profile is significantly varied with external parameters, such as silicon etch / sidewall passivation time, ion energy, and substrate temperature. The variation of fuorocarbon film properties was characterized for various process parameters. Deeply etched micro-structure on silicon mold was well transferred to polydimethylsiloxane (PDMS) and may be suitable for polymer embossing applications.

PS-MoP27 Instabilities of Nanoporous Silica (NPS) During Plasma-Based Pattern Transfer and Subsequent Resist Stripping*, **X. Hua**, T. Kwon, R. Phaneuf,* University of Maryland, College Park*; G. Oehrlein,* University of Maryland, College Park, US*; P. Lazzeri, M. Anderle,* ITC-irst, Italy*; P. Jiang,* Texas Instruments, Inc.*; C.K. Inoki, T.S. Kuan,* University at Albany, SUNY

We have investigated several instabilities of nanoporous silica associated with the fluorocarbon plasma-based transfer of resist masks and subsequent removal of the resist mask. Novel phenomena that are absent during plasma exposure of a homogeneous material, e.g. SiO@sub 2@, are observed for NPS materials as a result of the changes in the plasma surface interactions. These include changes in the morphology of near surface pores along with plasma-process dependent surface roughening of the NPS etching front. The instabilities are dependent on of both the plasma properties and NPS characteristics, e.g. overall porosity. The physical mechanisms giving rise to these instabilities in fluorocarbon-based plasma will be discussed based on plasma and surface characterization results. Resist mask removal can lead to deep modifications of NPS materials, e.g. carbon loss and an increased dielectric constant. We have investigated the potential of direct and remote plasmas fed with N@sub 2@/H@sub 2@/O@sub 2@ precursor gas mixtures and substrate temperature to maximize resist removal rate while minimizing NPS materials modifications.

PS-MoP28 Real-Time Etch Optimization in Electron Cyclotron Resonance-Microwave CO/H@sub 2@ and CO@sub 2@/H@sub 2@ Plasmas*, **A.A. Dyachenko**, A.S. Orland,* Auburn University*; R. Blumenthal,* Auburn Univerisity

Previous results, in our group@super 1@, have indicated that the etch rates of nickel are significantly enhanced when formic acid appears in CO/H@sub 2@ plasmas and when oxalates appear in CO@sub 2@/H@sub 2@ plasmas. At that point, it was not clear whether the formic acid and oxalates are new primary etchants or daughter ions of the metal complex product. In this work, a real-time monitoring of the concentrations of chemically generated species in electron cyclotron resonance (ECR) hydrogen plasmas is investigated by means of supersonic pulse plasma sample mass spectrometry. The influence of various plasma parameters, on the concentration of etching products/etchants and on the actual etch rates, has been examined with a -200 V DC bias at maximum brightness. Above 30% CO concentration, contamination of the vacuum chamber occurs and therefore experiments under such conditions have not been conducted. Upon decreasing the CO fraction from 30% to 5%, an increase on the order of 30% in the formic acid concentration was observed. Increasing microwave power from 150 W to 250 W results in a 20% increase in the formic acid concentration. Correlations and anticorrelations between the concentrations of reactive species formed in the plasma and the etch rates measured by profilometry will be presented along with a chemical mechanism consistent with the observed etch rate enhancement. Similar results for oxalates in CO@sub 2@/H@sub 2@ plasma will also be presented. @FootnoteText@ @footnote 1@ A.Orland, Ph.D. thesis, Auburn University, 2003.

PS-MoP29 Anisotropic Etching of Sio@sub 2@ Film and Quartz Plate Employing Anhydrous Hf*, **T. Fukasawa**,* Tokai University, Japan

Plasma etching technology has been widely used since the 1980s in the fabrication of ultra-large-scale integrated (ULSI) circuits. However, charged particles such as ions and electrons generate ion implantation to Si, have charge up damage to SiO@sub 2@ film and have low selectivity of the photoresist. On the other hand, HF gas is also widely used in a removal process of native SiO@sub 2@ films and in a cleaning process of a wafer as a dry process. Only chemical reactions are dominant in the reactions of HF gas etching and Si is not etched by HF gas, consequently, non-damaged, highly selective etchings of SiO@sub 2@ film and quartz plate can be achieved in HF gas etching. However, almost all reports about HF gas etching were isotropic etchings. When I investigated planarization technology employing anhydrous HF gas, very unique etching characteristics were observed when the etched depth of AHF gas etching was measured employing OFPR-800 as a photoresist. The stage temperature was set at 20° C and AHF gas was introduced to the chamber at a pressure of 30 Torr. After 15 min etching, AHF gas selectively etched the quartz surface just below the OFPR resist. In this etching, neither plasma nor ultraviolet light was used. A SiO@sub 2@ film below the photoresist, OFPR-800, was selectively etched with AHF gas. However, etch-stop was observed at the depth of 1.5 µm after 15 min. I found that the flow rate of HF gas and a high-pressure process were very effective with regard to this issue. When the flow rate of HF gas was increased to 4300 sccm, etching never stopped over 40 min and 20 µm in depth. The etched depth increased linearly with the increase in etching time. Both ZEP-520-22 and SAL-602-SR2 gave the same results. The etch-stop problem was considered to be mass-balance between the condensed layer below the resist and the gas phase. When AHF etched SiO@sub 2@ film on Si substrate, notching profile was observed during the over-etching process.

PS-MoP30 Self-Aligned Contact Etch Development for 90nm Technology Node*, **M.G. Sedigh**, H. Lee, J. Zhang,* Cypress Semiconductor*; J. Stinnett, A. Joshi,* Applied Materials, Inc.

Self-aligned contacts play a significant role in driving down the cell size in CMOS-based memories, in particular DRAM and SRAM. We present development results of self-aligned contact etch for SRAM 90 nm technology node. Requiring high SiO@sub 2@, Si@sub 3@N@sub 4@, P.R. selectivity and vertical profile, combined with constrained imposed on the process by using 193 nm P.R. and organic BARC (required for improving lithography process window) and ever-present need for well-formed big structures in open area (i.e. overlay measurement marks) form the boundary of our development efforts. Summary of development effort starting from early stage (tool selection, chemistry selection, CIP etc.) and resolving specific failure modes (striation, CD bias, reverse microloading, etc.) will be presented. Some shortcomings and deficiencies with current tool/architecture followed by our recommendation for eliminating them toward next generation dielectric etch will be also discussed.

PS-MoP31 Atomic Layer Etching of Silicon using a Low Angle Forward Reflected Ar Neutral Beam*, **S.D Park**, D.H. Lee,* Sungkyunkwan University, South Korea*; G.Y. Yeom,* Sungkyunkwan University, South Korea, Korea

Atomic layer etching (ALE) is expected to be a very important process for the fabrication of future nano-scale devices, because current dry etching techniques could not strictly control the etch depth in nono-scale because of their high etch rates. In addition, relatively high energy of the ions can damage the crystal surface. Therefore, many studies on ALE of Si have been reported in recent years to develop a technique to etch materials layer-by-layer. But, these previous methods may show charging damage due to the charged particles such as positive ions and photons generated in the plasma. Therefore, in this study, ALE of Si was carried out using a sequential Cl2 adsorption and an Ar neutral beam irradiation instead of ion beam. Low energy Ar neutral beam was generated by a low-angle forward reflected neutral beam technique. ALE of Si is a cyclic process consisting of 4 steps: (1) adsorption of Cl2 on Si surface, (2) evacuation, (3) Ar neutral beam irradiation to the surface, (4) evacuation of etch products. The etch process parameters for optimizing the atomic layer etching of Si are Cl2 gas exposure time, Ar neutral beam irradiation time, Ar neutral beam energy, etc. It is expected that the etch rate per cycle increased with the chlorine supplying time and saturated to a constant value of about 1.36â"« per cycle which corresponds to the one mono-layer thickness of Si. The surface damage was estimated using transmission electron microscopy (TEM). The step height divided by the total number of ALE cycles yielded the etch rate per cycle. A scanning electron microscope (SEM) was used to observe as-etched Si profiles and an atomic force microscope (AFM) was used to analyze the surface topography.

PS-MoP32 Vertical Platinum Etch Profile for Electrode of High-K Dielectric Materials with Cl@sub 2@/Ar/C@sub 4@F@sub 8@ Plasma*, **C.W. Kim**, H.-Y. Song, Y.H. Choi, S.G. Yang,* Inha University, South Korea*; J.G. Lee,* Bucheon College, South Korea*; S.-G. Lee, B.-H. O, I.H. Lee,* Inha University, South Korea*; S.-G. Park,* Inha University, South Korea, Korea, Republic of

In this paper, we investigate the characteristics of the platinum dry etch using Cl@sub 2@/Ar/C@sub 4@F@sub 8@ gas with ICP(Inductively Coupled Plasma) source. Platinum is widely used as electrode of high-k dielectric materials and the vertical side wall slope of electrode is important especially in the fine pattern process for ultra large scale integration. The etch selectivity of platinum to photoresist is improved from 1:1 to 1.6:1 by C@sub 4@F@sub 8@ gas addition to Cl@sub 2@/Ar gas and this leads to very anisotropic Pt sidewall etch angle of 80° even with the photoresist masking. We studied the C@sub 4@F@sub 8@ addition effect by monitoring the variation of active plasma species with QMA(Quadruple Mass Analyzer) and analyzing the residue of etched surface.

PS-MoP33 Process Consideration in MRAM Metal Etch*, **S. Kanakasabapathy**,* IBM T.J. Watson Research Center

Magnetic Random Access Memory (MRAM) holds the promise to evolve into a non-volatile universal memory@footnote 1@,@footnote 2@. The MTJ stack comprises of a top data storing magnetic film that is separated by a thin Tunnel Barrier in the order of 10A from a bottom magnet@footnote 3@. MTJ patterning involves etching of non-volatile magnetic alloys without the benefit of a high thermal budget. The sidewall redepositon of the etch products is a key yield detractor in these etches@footnote 4@. Besides tapering the profile to achieve sidewall cleaning, stopping on the very thin tunnel barrier is considered an option to minimize this detractor. We present in this paper, such options and contrast them. @FootnoteText@ @footnote 1@W.J. Gallagher et al,"Microstructured Magnetic Tunnel Junctions", Journal of Applied Physics, 81, p.3741 (1997).@footnote 2@S. Tehrani et al,"High Density Submicron Magnetoresistive Random Access Memory", Journal of Applied Physics, 85, 5882 (1999).@footnote 3@S.S.P Parkin et al, "Exchange Biased Magnetic Tunnel Junctions and Application to Nonvolatile Random Access Memory", Journal of Applied Physics, 85, 5828 (1999).@footnote 4@R. Ditizio et al, "Cell Shape and Patterning Considerations for Magnetic Random Access Memory (MRAM) Fabrication", Semiconductor Manufacturing Magazine, January 2004. .

PS-MoP34 A Zero-order Semi-Empirical Physical Model for Chemically-Enhanced Physical Vapor Deposition (CEPVD) of Ta(C)N}*, N. Li, **D.N. Ruzic**,* University of Illinois at Urbana-Champaign

Chemically-enhanced physical vapor deposition (CEPVD) is a new technique having the potentiality to deposit films with physical vapor deposition (PVD) quality and chemical vapor deposition (CVD) step coverage. A Ta target is sputtered in a magnetron system with the metal-organic precursor vapor, TBTDET, in combination with a reactive (N2) gas and a secondary RF plasma. CEPVD film properties have demonstrated wide range of variation with the processing parameters. For instance, by controlling the processing the film resistivity drops dramatically from nearly insulating to about 250 ï�-ï�-ï?-cm. Therefore a zero-order semi-empirical model is established correlating the processing parameters with the target and film surface coverage by Ta, TaN and organic sites, which predicts the target operation mode, and the film elemental composition. The physical component of the model involves the calculation of the plasma properties, reactive sputtering, transportation and deposition of the three kinds of surface sites. The chemical reactions are represented as elementary gas phase reactions enhanced by electron impact, H reducing and ion bombardment. The rate constants are derived by simulation curve fitting with the AES experimental data. The organic by-products accounting for the detection of carbon on the substrate by AES analysis and poisoning of the target are categorized into non-volatile product (OR1) and volatile product (OR2) in a lump-sum assumption. Simulation results are compared with the experiment data with different RF power, bias voltage, pressure, carrier gas flow rate, TBTDET vapor pressure etc, and the deviation is consistently below 25 %. For example, the simulation shows that at certain working conditions the carbon concentration decreases from 61% to 54% as the substrate voltage changes from 0V to -60V, which corresponds to the AES result that the carbon concentration decreases from 51% to 43%.

Surface Science

Room Exhibit Hall B - Session SS-MoP

Poster Session

SS-MoP1 Studies of Hydrogen on Pd{111} at 4 K Utilizing Scanning Tunneling Microscopy and Spectroscopy*, **L.C. Fernández-Torres**, E.C.H. Sykes, P. Han, S.U. Nanayakkara, P.S. Weiss,* The Pennsylvania State University

The interaction of hydrogen with Pd{111} has been investigated with low temperature scanning tunneling microscopy and spectroscopy. Palladium is unique in its ability to both adsorb and absorb hydrogen. Adsorption of low exposures of hydrogen has allowed for the observation of tip-induced hydrogen atom diffusion at 4 K. The diffusion of atomic hydrogen at 4 K has been ascribed to inelastic tunneling of electrons; inelastic electron tunneling spectroscopy (IETS) corroborates this assignment, and the hydrogen atom diffusion barrier has been determined. Adsorption of high exposures of hydrogen results in formation of two ordered overlayer structures: (1x1)-H and (@sr@3x@sr@3)-2H. Absorption of hydrogen into subsurface sites in Pd, concurrent with H diffusion from the bulk, have been attributed as the predominant reasons for two observed phenomena: tip-induced vacancy ordering, and Pd{111} lattice distortion.

SS-MoP2 Quartz Crystal Microbalance and Quadruple Mass Spectrometry Studies of Surface Reactions of @beta@-diketonate Precursors and O Radicals*, T.T. Van,* *J.P. Chang,* University of California, Los Angeles

Pure and Er-doped Y@sub 2@O@sub 3@ thin films are of interest for next generation of microelectronic and optoelectronic devices. In this work, a radical-enhanced atomic layer deposition (ALD) process was developed for synthesizing these materials. Specifically, quartz crystal microbalance (QCM) and quadruple mass spectrometry (QMS) were used to study the surface reaction kinetics of @beta@-diketonate precursors with O radicals. The @beta@-diketonate complexes chosen for this study are Tris(2,2,6,6-tetramethyl-3,5-heptanedionato) M(III), or M(TMHD)@sub 3@, where M = Y or Er. The temperature-controlled QCM was used to measure the real time mass changes, since each reaction steps in ALD cycles causes a specific mass increase or decrease. The evolution of surface species during the deposition was identified and analyzed by QMS. Similar adsorption and desorption kinetics were observed for both Y(TMHD)@sub 3@ and Er(TMHD)@sub 3@. The surface coverage increased with increasing substrate temperature then saturated. The adsorption isotherms were fitted with the simple Langmuir model and the adsorption rate coefficients were found to decrease with increasing temperature. Conversely, the desorption rate coefficients increased with increasing temperature. The apparent activation energies are ~0.25 eV. The desorption of volatile by-products during the O radical pulse resulted in a rapid mass decrease followed by saturation. The critical O radical dose needed to reach this saturation increased with increasing coverage and approached 2 minutes at high coverage. The O radicals, besides effectively remove the @beta@-diketonate ligands, were found to create reactive site for precursor adsorption. Specifically, the mass increase during a subsequent precursor pulse depended linearly on the preceding O radical pulse time. Finally, well-controlled atomic layer deposition of Er@sub 2@O@sub 3@ and Y@sub 2@O@sub 3@ was demonstrated.

SS-MoP4 Chemical Bonding of Saturated Hydrocarbons to Metal Surfaces*, **H. Öström,*** Stockholm University, Sweden*; L. Triguero,* KTH syd, Sweden*; M. Nyberg,* Stockholm University, Sweden*; H. Ogasawara,* Stanford Synchrotron Radiation Laboratory*; L.G.M. Pettersson, A. Nilsson,* Stockholm University, Sweden

We have investigated the electronic and geometric structure of saturated hydrocarbons adsorbed on metal surfaces using x-ray absorption spectroscopy (XAS) and x-ray emission spectroscopy (XES) in combination with density functional theory (DFT) spectrum calculations. XES, which probes the occupied density of states, reveals new adsorption-induced states, which we assign to interaction between the both occupied and unoccupied CH orbitals and the metal d-band. By performing a systematic investigation of how the XA and XE spectra are influenced by different structural parameters, we conclude that the geometry is significantly distorted relative to the gas phase. The bonding to the surface leads to strengthening of CC bonds and weakening of CH bonds. Comparison between different metals shows that the position of the metal d-band is important for the bonding to the surface. These results can be useful for the understanding of the CH bond cleaving mechanism, which is important in catalysis.

SS-MoP5 UHV Study of Cyclohexane on Zr(0001)*, **N. Stojilovic,*** *J.C. Tokash, R.D. Ramsier,* The University of Akron

We investigate the behavior of cyclohexane on Zr(0001) with temperature programmed desorption (TPD), Auger electron spectroscopy (AES) and low-energy electron diffraction (LEED) methods. Following 150 K adsorption cyclohexane dissociates at low exposures with no thermal desorption detected. Relatively broad desorption features (400-750 K) of the parent molecules are observed for higher exposures. The TPD profiles change with exposure, and the yields increase monotonically. AES reveals more carbon after annealing to 850 K than immediately after adsorption. Additionally, AES data indicate different forms of carbon before and after annealing. This work improves our understanding of the behavior of carbon impurities on Zr(0001), and of the influence of temperature-dependent surface-subsurface diffusion.

SS-MoP6 Study of the Low-Temperature CO+O@sub 2@ Reaction Over Pd and Pt Surfaces*, **E. Podgornov,*** University of California, Riverside*; A. Matveev, V. Gorodetskii,* Boreskov Institute of Catalysis, Russia*; F. Zaera,* University of California, Riverside

The kinetics of CO oxidation at low temperature has been studied with effusively-collimated molecular beams (MB) and reactive thermal desorption, combined with an isotope-labeling technique. High-resolution electron energy loss spectroscopy (HREELS), field electron microscopy (FEM), and photoelectron microscopy (PEM) have also been applied to determine the roles of subsurface atomic oxygen and surface reconstruction in self-oscillatory phenomena on Pd(111), Pd(110) and Pt(100) single crystals and on Pd and Pt tip surfaces. It was found that high local concentrations of adsorbed CO during the transition from a Pt(100)-hex reconstructed surface to the unreconstructed 1x1 phase apparently prevents oxygen atoms from occupying hollow sites on the surface, and leads to the formation of a weakly-bound adsorbed atomic oxygen. It was inferred from MB experiments with oxygen isotope that the weakly-bound atomic oxygen is the active form that reacts with CO to form CO@sub 2@ at T = 140-160 K. In the experiments involving FEM, sharp tips of Pd and Pt were used to perform in situ investigations of dynamic surface processes. It was concluded that non-linear reaction kinetics is not restricted to macroscopic planes, since planes as small as 200 Å in diameter show the same non-linear kinetics as larger flat surfaces; regular waves appear under oscillatory reaction conditions and propagate through adjacent crystal nanoplanes because of an effective coupling between them. Additional results from isotope-labeling MB experiments led to the conclusion that adsorbed weakly-bound atomic oxygen, and not "hot" oxygen adatoms (excited transient states of adsorbed oxygen which may appear due to excess energy after the dissociation of O@sub 2@), is the active form of oxygen that reacts with carbon monoxide at low temperatures.

SS-MoP7 Adsorption and Reaction of Butyl Groups on Pt(111)*, **I. Lee,*** *F. Zaera,* University of California, Riverside

The adsorption and thermal reaction of 1- and 2-butyl moieties on Pt(111) was investigated by using reflection-absorption infrared spectroscopy (RAIRS) and temperature-programmed desorption (TPD). The butyl intermediates were prepared via thermal activation of the C-I bond of 1- and 2-iodobutanes, respectively. Buta-1,2-diyl and buta-2,3-diyl were observed after the first dehydrogenation. The subsequent thermal activation of those butyl groups resulted in a competition between reductive elimination to butane and @beta@-hydride elimination to butene. Coadsorption experiments with hydrogen and deuterium were used to characterize hydrogenation and H-D reactions. It was found that the hydrogenation of 1-butyl to butane is enhanced by predosed hydrogen, while 2-butyl favors the dehydrogenation to butene via @beta@-hydride elimination.

SS-MoP8 Wetting Behavior of Liquids and Polymer Solutions on the Micro-patterned Fluoroalkylsilane Monolayer Surfaces*, **A. Takahara,*** *M. Morita, J. Fukai, H. Ishizuka,* Kyushu University, Japan

Micropatterned fluoroalkylsilane monolayers were fabricated on a Si-wafer substrate by chemical vapor adsorption (CVA) of fluoroalkyltrialkoxysilane and vacuum ultraviolet (VUV)-ray photodecomposition under photomask with line-pattern. Field-emission scanning electron microscopic (FESEM) and atomic force microscopic(AFM) observations revealed that the micropatterned surface of fluoroalkylsilane and bare Si-wafer corresponding to the line-width of photomask was formed. Dynamic and static contact angle measurement revealed the anisotropy of water contact angles parallel and perpendicular to the line direction. Droplets of solution of polystyrene were deposited on the line-pattern by inkjet process from the orifice with a diameter of 50ï�-m It was revealed that the xylene solution was repelled from the oleophobic fluoroalkylsillane surface and the PS stripe corresponding to the line pattern shape was obtained.

SS-MoP9 Solvent and Chain Length Dependence of the Conformational Order in Self-Assembled Dialkylammonium Monolayers on Mica*, **G. Haehner,*** University of St Andrews, United Kingdom, UK*; M. Zwahlen,* University of St Andrews, United Kingdom*; W. Caseri,* ETH Zurich, Switzerland

The adsorption of cationic surfactants, for example alkylammonium compounds, can be employed to modify the surface properties of layered silicates, such as micas and clays. This process is of significant importance to many industrial applications, ranging from ore flotation in the mining industry and soil treatment to the pharmaceutical, household, food processing and cosmetics industry. The conformational order in adsorbed monolayer coatings is an important parameter for the reliable use of the layers. Dialkylammonium films on mica substrates prepared via ion exchange in solution can exhibit a high degree of order and orientation, similar to thiol-gold systems. We have studied the quality of such films on mica depending on the solvent and the alkyl chain length. Contact angle measurements, photoelectron spectroscopy (XPS) and near edge X-ray absorption fine structure spectroscopy (NEXAFS) were employed to characterize the adsorbed layer. A remarkable difference in the established conformational order was observed for films prepared from different solvents and with different chain lengths.

SS-MoP10 Single Step Functionalization of Scribed Silicon with Acid Chlorides and Epoxides*, C.A. Pew*, *Y.-Y. Lua, W.J.J. Fillmore, M.R. Linford,* Brigham Young University

A perpetual problem in surface modification and functionalization is that of finding better and more convenient ways for creating reactive functional groups on surfaces. Two reactive functional groups of great importance in surface modification, and in organic chemistry in general, are the epoxide ring and the acid chloride group. Here we report that epoxide- and acid chloride-terminated monolayers on silicon can be prepared in a single step by chemomechanically scribing silicon that is wet with a bifunctional epoxide (1,2,7,8- diepoxyoctane) or an acid chloride (adipoyl chloride). Surface modification takes place in an open laboratory with compounds that have not been degassed. We also describe the amine-reactivity of these monolayers, using X-ray photoelectron spectroscopy, time-of-flight secondary ion mass spectrometry, and wetting to prove surface functionalization. Finally, we show that the amine reactivity in these monolayers can be controlled and improved by making mixed monolayers composed of a shorter-chain monofunctional adsorbate and a longer-chain bifunctional adsorbate.

SS-MoP11 Chemical Functionalisation of High Porosity, Nanostructured Thin Films*, S. Tsoi*, *E. Fok, J.G.C. Veinot, J.C. Sit,* University of Alberta, Canada

In sensing and catalysis applications, controlled interaction of nanostructured materials with the outside environment is essential. Control over both the structure and the surface properties of these nano-materials allows optimisation for a wide range of applications. Using an advanced technique known as glancing angle deposition (GLAD)@footnote 1@, we can grow porous thin films with controlled nanostructure and a high surface area easily accessible from the surrounding environment. These structural properties make GLAD films highly suitable for sensing and catalysis; the surface properties can then be controlled through chemical functionalisation. Siloxane-based self-assembly@footnote 2@ has been demonstrated as an effective means for functionalisation of a wide variety of simple flat and freestanding structures. Our work is the first application of this technique to the complex, porous, three-dimensional nanostructures grown using GLAD. Goniometer measurements on as-deposited films (hydrophilic, 0° advancing aqueous contact angle) and films treated with various trichlorosilanes (R-SiCl@sub 3@) (hydrophobic, ~120° contact angle) support a substantial modification of the hydrophilicity of the GLAD film surfaces. X-ray photoelectron spectroscopy and standard electrochemistry measurements confirm that the siloxane-based self-assembly process effectively penetrates the GLAD film surface, allowing complete functionalisation of the 3D structures and underlying substrate. Of particular importance, varying degrees of hydrophilicity of the GLAD structures can be achieved by further functionalising the tail groups of the assembled molecule. Such flexibility in the self-assembly process allows the surface chemistry of GLAD films to be extensively tailored for specific requirements of a wide range of applications. @FootnoteText@ @footnote 1@ K. Robbie and M.J. Brett, J. Vac. Sci. Technol. A 15 (1997).@footnote 2@ J.E. Malinsky, J.G.C. Veinot, et al., Chem. Mat. 14 (2001).

SS-MoP13 Organic Molecules Self Organization on Metal Surfaces and on Insulator Thin Films*, L. Ramoino*, *M. Von Arx, S. Schintke,* University of Basel, Switzerland*; T.A. Jung,* Paul Scherrer Institute and University of Basel, Switzerland*; H.-J. Güntherodt,* University of Basel, Switzerland

Single molecules on surfaces are promising objects to overcome the limits of current silicon based techniques. Molecular properties like self assembling and preferential adsorption are specially interesting in order to evolve from top-down manufacturing methods to bottom-up techniques. Formation of a wide variety of molecular self organized structures has been achieved on metal and semiconductor surfaces. Much less is known about the adsorption and self organization of organics molecules on insulators. However, decoupling molecules from the conductive substrate and building-up metal-insulator as well as semiconductor-insulator patterns is very interesting in the perspective of molecular electronics. It has been shown as STM and STS are profitable tools to study morphology and electronic structure of ultra-thin insulating structures on booth metallic and semiconductor substrates. In addition, by mean of insulating films it should be possible to tune the molecule sample interaction by varying the thickness of the insulating layer. We are studying the growth of ultra-thin NaCl films on different metal surfaces. STM pictures clearly show the formation of ordered 2D islands between 1 and 3 monolayer thick and with a characteristic square shape. Their size can be reliably controlled in a range between a few and hundreds of nanometers. Self-organization of different organic molecules deposited on the NaCl/metal system, has been studied for various molecule substituents and surface coverages. The possible molecule-surface interactions leading to self-assembled molecular structures on ultra-thin insulators are discussed for the different molecules and coverages in comparison.

SS-MoP14 Low Energy Electron Diffraction Study of Dodecanethiol Self-Assembled Monolayers Grown on Pt(100) and Pt(111) by Vapor Deposition*, T.M. Sweeney*, *P.S. Robbert, C.A. Ventrice, Jr.,* University of New Orleans*; H. Geisler,* Xavier University

One of the most popular substrates for growing self-assembled monolayers (SAMs) is the Au(111) surface. This is primarily due to the fact that it does not oxidize during preparation of the SAMs from solution. However, gold is not compatible with conventional Si-based electronics due to its tendency to diffuse into Si. A more promising candidate for the integration of SAMs with Si-based electronic devices is the use of Pt for the growth of the SAMs. Therefore, we have performed a study of the growth of dodecanethiol SAMs on single-crystal Pt(100) and Pt(111) surfaces by vapor deposition in ultra-high vacuum. The clean Pt(100) surface exhibits a four-domain (5x1) reconstruction. Upon deposition of ~0.1 L of thiol, the (5x1) reconstruction is removed. Doses greater than a few Langmuir result in a weak (1x1) pattern, indicative of the growth of a disordered thiol overlayer on the unreconstructed Pt(100) surface. The clean Pt(111) surface does not exhibit a surface reconstruction. Deposition of ~0.1 L of thiol results in a sharp (2x2) LEED pattern, which indicates that the initial sticking coefficient is near unity and that the thiol molecules most likely have a standing up geometry. As with the Pt(100) surface, doses beyond a few Langmuir result in the formation of a weak (1x1) LEED pattern. In addition, we have initiated a study of the electronic properties of these SAMs using angle-resolved photoelectron spectroscopy. The results of these measurements will also be presented.

SS-MoP16 Thermal Decomposition of Generation 4-Polyamidoamine Dendrimers Films: Decomposition Catalyzed by Dendrimer-Encapsulated Pt Particles*, O. Ozturk*, *T.J. Black, F. Parsons, K. Pizzolato, J.S. Ratliff, C.T. Williams, D.A. Chen,* University of South Carolina

The thermal decomposition of hydroxyl terminated generation-4 polyamidoamine dendrimer (G4 OH) films deposited on Au surfaces has been compared with decomposition of the same dendrimer encapsulating a ~40-atom Pt particle (Pt-G4OH). Infrared spectroscopy studies showed that when the films were heated in air to various temperatures up to 275° C, the disappearance of the amide vibrational modes occurred at lower temperature for the Pt-G4OH film. Dendrimer decomposition was also investigated by thermogravimetric analysis (TGA) in both air and argon atmospheres, and decomposition of the dendrimer films on Au surfaces was studied by temperature programmed desorption (TPD) and X-ray photoelectron spectroscopy (XPS) under ultrahigh vacuum conditions. For both G4OH and Pt-G4OH films, heating to 100° C resulted mainly in the desorption of small molecules such as H@sub 2@, H@sub 2@O, CO and CO@sub 2@. Heating the G4OH films to 200° C induced the desorption of larger dendrimer fragments around 72, 84, 98, 127, 146 and 261 amu. For the Pt-G4OH films, mass fragments above 98 amu were not observed at any temperature, but much larger intensities for H@sub 2@ desorption were detected compared to that for the G4OH film. XPS studies of the G4OH films demonstrated that nearly all of oxygen and nitrogen atoms were removed from the surface after heating to 450° C. For the Pt-G4OH dendrimer films, most of the oxygen was also removed after heating to 450° C, but there was little decrease in the intensities of the carbon and nitrogen signals. All of these results are consistent with the fact that the Pt particles inside the G4OH dendrimer catalyze thermal decomposition, allowing dendrimer decomposition to occur at lower temperatures. However, the Pt particles also catalyze bond scission within the dendrimer fragments so that greater concentrations of atomic carbon and nitrogen remain on the surface after heating the dendrimer films in vacuum.

SS-MoP17 Spontaneous Molecular Row Formation of 9,10-Thiolated Anthracene on Cu(111)*, K.-Y. Kwon*, *X. Lin, G. Pawin, K. Wong, B.V. Rao, L. Bartels,* University of California, Riverside

Self-assembled monolayers (SAMs) have been the subject of intense research for the recent two decades due to the fact that they can be used to dramatically modify the chemical, physical and electronic properties of surfaces. Thiolate-SAMs offers powerful opportunities for fundamental studies of electron transport, single molecule devices, control of surface wettability, etc. It is known that both alkane- and arene-thiols stand close to upright on the surface at high coverage. Here, we report on the adsorption structure of 9,10-(diacetylthio)anthracene on Cu(111) at low temperatures in ultrahigh vacuum using scanning tunneling microscopy (STM). Before deprotection of the acetyl group, the molecules are mobile even at 80K. Upon heating of the sample in excess of 180K, the acetyl protection group is removed from the thiol and desorbs, as ascertained by thermally programmed desorption experiments. After renewed cooling of the sample to 80K, we find spontaneous assembly of extended molecular rows of dithioantracene molecules. Studies of the attachment and disattachment of diffusing molecules to the end of the rows at various cryogenic temperatures indicate a barrier of 14.8KJ/mol for this process. At increased coverages the antracenes form extended island with a rectangular unit cell.

SS-MoP18 Effect of Nitrogen Addition on the Liquid Crystal Alignment from Hydrogenated Amorphous Carbon*, **H.J. Ahn**, K.C. Kim, J.B. Kim, H.K. Baik, C.J. Park, J.Y. Hwang, H.K. Kang, D.S. Seo,* Yonsei University, Korea

In order to control the alignment of nematic liquid crystal (LC), nitrogen addition to the hydrogenated amorphous carbon thin films was investigated. The hydrogenated amorphous carbon layer had been developed the novel inorganic alignment layer for ion beam (IB) irradiation method. The IB method preserved some damage of the alignment layer since it was the non-contact alignment type. However, the low pretilt angle and the weak anchoring force were pointed out the vulnerable points. The alignment layer was deposited by plasma enhanced chemical vapor deposition (PECVD), and the nitrogen addition to the amorphous carbon layer could cause the change of pretilt angle. XPS and the contact angle were measured for analysis of the alignment layer and polarized optical microscope (POM) and pretilt angle measurement instrument were used to estimate the LC cells.

SS-MoP19 The Coadsorption of Mercury and Molecular Icosahedra on Cu(100)*, **C.C. Ilie**, L.G. Rosa, S. Balaz, B. Doudin, P.A. Dowben,* University of Nebraska-Lincoln

Mercury and alkali metal mixtures with molecules have a long history in the study of non-metal to metal transitions. Using photoemission and electron energy loss spectroscopy, we have investigated the changes in the electronic structure of molecularly adsorbed orthocarborane films as a function of Hg co-adsorption. Two scenarios for co-adsorption of Hg and the icosahedral molecule closo-1, 2 dicarbadodecaborane (orthocarborane) are considered. The mercury atoms may form a lattice which weakly interacts with orthocarborane lattice, or Hg may form a layer between the Cu substrate and orthocarborane molecular film. Mercury 5d@sub 5/2@ shallow core level widths in photoemission suggest interaction with the molecular film, but the binding energies of the molecular orbitals induced photoemission feature suggest that the interaction is weak.@FootnoteText@D. N. McIlroy, Jiandi Zhang, P. A. Dowben, P. Xu and D. Heskett, "Surface Science", 328, 47-57 (1995)

SS-MoP21 Reactivity of Metal Carbide Surfaces and Nanoparticles: a Density Functional Study*, **P. Liu**, J.A. Rodriguez, J.T. Muckerman,* Brookhaven National Laboratory

The destruction of S-containing molecules is a very important issue in the chemical industry and the control of environmental pollution. The reactivity of metal carbide surfaces, M@sub2@C(001) (M=Ti,V,Mo) and MC(001), as well as M@sub8@C@sub12@ (metallocarbohedrene, metcar in short) nanoparticles towards sulfur, sulfur dioxide and thiophene was investigated using density functional theory. Our study reveals unexpected ligand and steric effects. Due to the corner or edge sites (ligand effect), the M@sub8@C@sub12@ nanoparticle behaves as active as M@sub2@C(001) towards sulfur and sulfur dioxide in spite of the high C/M ratio and C@sub2@ groups. Spontaneous S-O bond cleavage was observed on both M@sub8@C@sub12@ and M@sub2@C(001). In contrast, these adsorbates bond weakly with MC(001), and there is an activation barrier for the decomposition of SO@sub2@ on MC(001). Contrary to common assumptions, the C atoms are not simple spectators and play a key role in the energetics for the dissociation of sulfur dioxide. In the case of thiophene adsorption, only M@sub2@C(001) exhibits a high reactivity that leads to a spontaneous S-C bond cleavage. The interaction of thiophene with both MC(001) and M@sub8@C@sub12@ is weak. On the nanoparticle, steric repulsion between the C@sub2@ groups and thiophene overcomes the high reactivity of the Mo atoms in corner or edge sites (ligand effect). Our results illustrate the complex interplay of ligand and steric effects in nanoparticles of metal compounds.

SS-MoP22 Adsorption of Hydrogen on CNT Surfaces and Surface Chemistry on HOPG*, **J. Nakamura**, E. Yoo, M. Ishihara, T. Habe, N. Yagai, E. Matsuyama, T. Matsumoto,* University of Tsukuba, Japan

Hydrogen storage by carbon nanotubes, graphite and the other carbon materials have been studied from the viewpoints of chemisorption of hydrogen at atmospheric pressure. We find that deposited Pd nanopraticles and formation of defects produced by oxidation increased the chemisorption of H atoms (2 - 4 wt%) on CNT surfaces. IR spectra showed peaks assigned to CH@sub 2@ . Desorption of hydrogen was observed around 700 K. In order to study the site of hydrogen on carbon surfaces with scanning tunneling microscopy (STM), we used highly oriented pyrolytic graphite (HOPG) surfaces as a model surface. The hydrogen adsorption is not observed on a clean HOPG surface by STM after dosing H2 or atomic H at 300 K. Temperature programmed desorption (TPD) experiment gives no desorption peak and small desorption peak of H@sub 2@ (m/e=2) at ~570 K assignable to H atoms adsorbed at step edges. Defects are produced on HOPG by Ar ion sputtering and annealing at 1173 K. Bright hillocks are observed by STM, and are assigned to pits in graphene sheets due to high local density of states of sp3-like dangling bonds produced by removing adjacent carbon atoms. After dosing atomic H on the defective HOPG at 300 K, the STM topographs show dark lines on the bright hillocks. The average height of the hillock also decreases from 0.71 nm to 0.32 nm. The average height of the hillocks is recovered to 0.69 nm by heating the sample to 873 K where H desorbed fully from the HOPG surface on a TPD spectrum. These results indicate that the atomic H adsorbed on the defect sites at 300 K, and the local density of states was lowered around the pits.

SS-MoP23 An in situ XPS Study of Fresh Hydrogenated Amorphous Carbon Films*, **Y. Yun**, A.J. Gellman,* Carnegie Mellon University

In order to develop vapor phase lubrication of hydrogenated amorphous carbon (a-CHx) films for use in hard disk manufacturing insights are needed into the fundamental surface chemistry of vapor deposited lubricants. In vapor phase lubrication, fresh a-CHx will be exposed to lubricants directly. Unfortunately, our current understanding of lubricant surface chemistry on a-CHx is based on studies performed on air-exposed, oxidized a-CHx films. Magnetron sputtering has been used to deposit films in ultra-high vacuum under varying conditions. These films have been characterized by Raman spectroscopy to show that they have characteristics similar to those used commercially. X-ray photoelectron spectroscopy (XPS) was used to study the oxidation of fresh a-CHx during controlled exposure to O2. The film surface saturated at ~20% oxygen after a 20 hour exposure to O2 at 10-4 Torr. One can estimate that under atmospheric conditions where the partial pressure of O2 is roughly 200 Torr, the a-CHx film will be oxidized in a few milliseconds. Thus oxidation of a-CHx is unavoidable between removal of the media from vacuum and dip-coating with lubricant.

SS-MoP24 Experimental Study of Cluster Size Effects on Damage Formation by Size-selected Gas Cluster Ion Beams*, **N. Toyoda**, I. Yamada,* University of Hyogo, Japan

A size-selected gas cluster ion beam (GCIB) system has been developed to study the size effects of energetic large cluster ion bombardments on a solid surface for the first time. This system equipped a permanent magnet with a magnetic flux density of 1.2 T. There is a sliding detector and sample holder on a guiding rail perpendicular to the incoming cluster beam axis. By locating a sample at a certain position, particular size of cluster ion can be irradiated continuously with affordable ion current density. With this magnetic filter, the cluster size distribution became 1/20 of those obtained in the conventional GCIB systems. Cluster size effects on damage formations in Si substrates were studied with the size-selected cluster ion beams. When the total acceleration energy of Ar-GCIB was 5keV, both amorphous and oxide thickness on Si substrate increased with decreasing cluster size. In the case of cluster size above 10,000, the irradiation damage in Si was dramatically reduced. This result showed good agreement with that obtained from molecular dynamics simulations. It indicated that very low-damage surface processing can be possible by controlling both the acceleration energy and the cluster size.

SS-MoP25 Plasma Base Ion Implantation Sterilization Technique and Ion Energy Estimation*, **S. Watanabe**,* Soken Kogyo Co., Ltd, Japan*; T. Tanaka,* Hiroshima Institute of Technology, Japan*; K. Shibahara, S. Yokoyama,* Hiroshima University, Japan*; T. Takagi,* Hiroshima Institute of Technology, Japan

Plasma base ion implantation (PBII) with negative voltage pulses to the test specimen has been applied to the sterilization process as a technique suitable for three-dimensional work pieces. Pulsed high negative voltage

(5µs pulse width, 300 pulses/s, -800 V to -13 kV) was applied to the electrode in this process at a gas pressure of 2.4 Pa of N@sub 2@. We found that the PBII process reduced the numbers of active Bacillus pumilus cell using N@sub 2@ gas self-ignitted plasma generated by only pulsed voltages. The number of bacteria survivors was reduced by 10@super -5@ x with 5 min exposure. As the ion energy is the most important processing parameter, a simple method to estimate the nitrogen ion energy calculated using distribution for nitrogen in Si implanted by PBII was developed. The implanted ion energy is discussed from the SIMS in depth profile.

SS-MoP26 Size-Dependent Resonant Inelastic X-ray Scattering of Ligand-Stabilized Cobalt Nanoparticles in Liquid Suspension*, H. Liu,* Lawrence Berkeley National Laboratory*; G. Thornton,* University College London, UK*; J.-H. Guo,* Lawrence Berkeley National Laboratory*; Y.D. Yin,* University of California, Berkeley*; A. Augustsson, C.L. Dong,* Lawrence Berkeley National Laboratory*; A.P. Alivisatos,* University of California, Berkeley*; D.F. Ogletree, M. Salmeron,* Lawrence Berkeley National Laboratory

The electronic properties of cobalt nanoparticles suspended in liquid have been investigated using synchrotron-based resonant inelastic x-ray scattering (RIXS) spectroscopy. Cobalt nanoparticles of 3, 4, 5, 6, and 9 nm were synthesized using wet-chemical methods. Liquid suspensions of the samples were then sealed into a vacuum-compatible cell closed with an x-ray transparent silicon nitride window, which separated the liquid from the surrounding vacuum during measurements. The experiments were carried out at beamline 7.0.1 of the Advanced Light Source (ALS). Particle oxidation was prevented by performing spectroscopy under the conditions of synthesis. RIXS spectra revealed two main features with energy losses of 1.8 eV and 6 eV. The 1.8 eV feature was assigned to excitations from the ground state to a final state dominated by the 3d@super n@ configuration electrons (dd transition), while the 6 eV feature was assigned to charge transfer from the ligand/solvent molecules to metal atoms with a 3d@super n+1@L@super -1@ final state. RIXS spectra excited at the Co 2p@sub 3/2@ XAS peak position showed that the intensity of the 1.8 eV peak (dd excitation) decreased with decreasing particle size. The charge transfer feature also shifted significantly, from ~ 6.9 eV for 9 nm nanoparticles to ~ 6.0 eV for smaller particles. This difference can be attributed to changes in the interaction between the metal core and the ligand/solvent molecules with nanoparticle size.

SS-MoP27 Design of a High-Speed Digital Feedback Loop for Scanning Tunneling Microscope Applications*, E. Ulin-Avila,* *A. Liu, B.V. Rao, L. Bartels,* University of California, Riverside

We present the development of a digital feedback loop for Scanning Tunneling Microscope (STM) operation that is capable of updating the tip height and xy position at a frequency of 170kHz. This feedback frequency approximates the maximum update rate of standard 16bit AD/DA converters of 200kHz. Its digital nature allows for precise linearization of the exponential dependence of the tunneling current on the tip-sample separation thereby avoiding oscillatory behavior common with non-linearized feedback loops. In addition, the digital setup allows full control of the z-motion of the tip at any point in time, which permits versatile tip control during lateral manipulation and rapid spectroscopy. The feedback loop incorporates a commercial digital signal processor board (Innovative Integration) utilizing a TI C6200 processor. First application of the new system will be presented.

SS-MoP28 Potential-induced Surface Stress at the Solid-liquid Interface Measured with a Differential Microcantilever-based Sensor*, V. Tabard-Cossa,* *M. Godin,* McGill University, Canada*; L.Y. Beaulieu,* Memorial University, Canada*; R.B. Lennox, P. Grutter,* McGill University, Canada

We report on a differential microcantilever-based system capable of measuring surface stress changes which occur during electrochemical reactions. Our system is composed of two microcantilever sensors. The first active microcantilever serves as the working electrode (in a conventional three-probe electrochemical cell configuration) and as the mechanical transducer (bending of the microcantilever), yielding simultaneous, real-time, in situ measurements of the current and interfacial stress changes. A second microcantilever serves as a reference sensor to detect any unwanted cantilever deflection resulting from temperature variations, mechanical vibrations and/or uncontrolled chemical reactions. This micromechanical cantilever sensor has a deflection sensitivity of 0.2 nm, which translates to a surface stress sensitivity of 1x10@super -4@ N/m with a dynamic range up to 50 N/m. This system is used to study the potential-induced surface stress at the solid-liquid interface for the case Au in 0.1 M HClO@sub 4@. The dependence of surface stress on surface charge density is examined for different Au surface morphologies. The role played by the morphology of the sensing substrate in microcantilever sensors is studied in order to understand the origin of the surface stress responsible for the sensor's response.

SS-MoP29 Selective Detection of Cr(VI) Using a Microcantilever Electrode Coated with a Self-Assembled Monolayer*, F. Tian,* Oak Ridge National Laboratory*; V. Boiadjiev,* University of Tennessee in Knoxville*; L. Pinnaduwage, G. Brown, T. Thundat,* Oak Ridge National Laboratory

We have demonstrated detection of Cr(VI) ions using functionalized cantilevers under electrochemical control. Au-coated microcantilever working electrodes are modified with self-assembled monolayer of 4-mercapto-pyridinium in sulfuric acid solution. Differential surface stress changes at the modified microcantilever have been measured to determine Cr(VI) by monitoring the potential-induced deflection of the microcantilever and simultaneous current-potential response by cyclic voltammetry. In an electrolyte containing sulfuric acid alone, the increase of potential causes a compressive surface stress resulting in the microcantilever bending away from monolayer coated Au side. Stressogram (first derivative of stress with respect to potential vs electrode potential) shows sweep rate independence, which is consistent with voltammetry. In the presence of 10@super -4@ M Cr(VI), a compressive stress peak can be observed during cathodic sweep. Surface stress characteristics continue to change during potential cycling at each fix sweep rate although the measured current-potential responses in the voltamogram are still constant. It suggests that there is a strong adsorption of Cr(VI) on pyridinium monolayer coated microcantilever electrode. Because of the adsorption of Cr(VI), the stressogram behavior is only consistent with voltamogram in the very beginning of sweep cycling and at much higher sweep rates. Our results demonstrate that the observed changes of differential surface stress are due not only to potential change, but also to ion adsorption/desorption and electron exchange at the electrode surface. Such potential controlled microcantilever technique offers new insights into the behavior of the solid-liquid interface during electrochemical reactions at modified electrodes.

SS-MoP30 Formation of Supramolecular Cavitands on Electrode Surfaces, *C. Safarowsky, A. Rang, C.A. Schalley, K. Wandelt,* ***P. Broekmann,*** University of Bonn, Germany

Supramolecular host-guest recognition is one the most challenging topics in modern chemistry and physics as well. Combining supramolecular approaches with state of the art surface science techniques allows to gain new insights about the structure and dynamics of supramolecular assemblies which are adsorbed at surfaces. In this contribution we present two approaches to realize supramolecular architectures at electrode surfaces in an electrochemical environment. The most prominent property of these architectures is their molecular host-cavity in which smaller guest molecules can be incorporated. Our method of choice to investigate these electrochemically fabricated arrays of host assemblies is the in-situ scanning tunnelling microscopy. Our first approach is based on the selforganization of small monomers to supramolecular assemblies at the surface. For this purpose we use redox-active dibenzyl-viologen cations which arrange on a chloride modified Cu(100) surface with the formation of square-shaped host assemblies consisting of 4 individual molecules. Characteristically, these assemblies are chiral and, hence, occur in two mirror-domains on the electrode surface. Our second approach is based on the direct adsorption of pre-assembled supramolecular units at the electrode surface from the solution phase. For this purpose we use so called Fujita-squares which are characterized by a fourfold-symmetric arrangement of 4 Pt(II)-cations stabilized by 4 bipyridine ligands and 4 further ethylenediamine molecules. These cationic molecules can also be adsorbed on a chloride modified Cu(100) electrode surface. In both cases we end up with molecular cavities which are oriented towards the solution phase and can, thus, be directly imaged by in-situ STM. The size of these cavities amounts to 1 nm in both cases.

SS-MoP31 Low Temperature Ultra-High Vacuum Scanning Tunneling/Force Microscopy for Single-Molecule Imaging and Spectroscopy*, T. Shimizu,* University of California, Berkeley*; A. mugarza,* Lawrence Berkeley National Laboratory, University of California*; Y. Qi,* University of California, Berkeley*; M. Heyde, D.F. Ogletree, M. Salmeron,* Lawrence Berkeley National Laboratory, University of California

A low temperature ultra-high vacuum scanning tunneling/force microscope (LT UHV STM/SFM) has been designed and constructed for imaging, spectroscopy, and manipulation at the atomic scale. This microscope is capable of operating in either STM or SFM modes through in-situ tip exchange. In addition, simultaneous STM/SFM is also possible using a conductive SFM tip. Our goal is to investigate inter- and intra-molecular forces between small molecules on metal surfaces, to explore the relation between electronic and mechanical properties, and to perform electronic, vibrational, and force spectroscopy. Preliminary STM images and scanning tunneling spectra of single-molecules will be presented.

SS-MoP32 Extracting Single Molecule Statistics from Scanning Probe Images*, B.A. Mantooth,* *E.C.H. Sykes, P. Han, P.S. Weiss,* The Pennsylvania State University

Scanning probe microscopes have enabled the unprecedented real-space visualization of single molecules and atoms on surfaces. Analyses of time-resolved sequences of these images allow the quantification of site-specific interactions and dynamics of adsorbed species. We have used scanning tunneling microscopy to probe and to quantify the weak substrate-mediated interactions in benzene overlayers on Au{111} at 4 K, and to characterize concerted motions of molecular cascades in these benzene overlayers. We use similar techniques to characterize the correlation of CO adsorption site with the charge density waves of the surface state of Ag{111}.

SS-MoP33 Site-selective Electroless Plating on Amino-terminated Diamond Substrate Patterned by 126 nm Vacuum Ultraviolet Light Lithography*, A. Hozumi,* National Institute of Advanced Industrial Science and Technology, Japan*; N. Shirahata,* National Institute of Materials Science, Japan*; S. Asakura, A. Fuwa,* Waseda University, Japan*; Y. Yokogawa, T. Kameyama,* National Institute of Advanced Industrial Science and Technology, Japan

The use of diamond substrates to manage heat dissipation in microelectronics has recently attracted considerable attention. Diamond metallization technique is of crucial importance in order to fabricate microelectronics devices. However, due to its excellent chemical inertness, it is hard to fabricate metal circuitry on the diamond substrates. Here we report a spatially defined metallization of copper (Cu) through an electroless plating on the amino-terminated diamond surface micropatterned by vacuum ultraviolet (VUV) photolithography. A diamond surface was first photochemically hydrophilized using VUV light of 126 nm. Due to VUV irradiation, the diamond surface became completely hydrophilic with its water-contact angle changing from 102° to 5° or less. According to X-ray photoelectron spectroscopy, polar-functional groups, such as C-O and C=O/O-C-O, were formed on the surface. Amino-terminated organosilane molecules were then chemisorbed onto the photochemically modified surface through a vapor phase. Next, the sample was exposed to 126 nm VUV light through a mesh mask, and subsequently immersed into a PdCl@sub 2@ solution kept at pH 5 for 30 min and rinsed with Milli-Q water. Finally, the substrate was immediately immersed into a commercial electroless Cu plating bath for 2 min at room temperature. Cu film with about 40 nm thick was site-selectively deposited onto the amino-terminated surface and remained free of deposits in the VUV-irradiated regions, as evidenced by an optical microscopy. The well-defined Cu microstructures were successfully formed on the diamond surface. Due to thermal treatment at 200 °C for 3 h in vacuum, a resistivity of the Cu film decreased from 17.1 µ@ohm@ cm to 13.4 µ@ohm@ cm.

SS-MoP34 Nanotribological Effects of Hair Care Products and Materials on Wet and Dry Human Hair using AFM/IFM, *C. LaTorre,* The Ohio State University*; **B. Bhushan,*** The Ohio Sate University

Tribological properties such as friction have been well studied for hair and other biological materials on the macroscale. Lower macroscale coefficient of friction values have been reported in literature for hair treated with various conditioning agents, as opposed to untreated virgin hair. The mechanisms behind lower friction with the application of conditioning products are understood on the macroscale level. However, the interactions between hair and hair care products that occur on the micro/nano scale and the tribological effects of these interactions are not as well understood. Major sources of investigation for treated hair includes localization of various conditioning products, mechanisms behind changes in friction and adhesion on the nanoscale due to conditioner agents, and how the products change the microstructure of the cuticle. The paper presents nanotribological studies investigating adhesion and friction using AFM/LFM. Test samples include Caucasian, Asian, and African hair at virgin and treated conditions in both wet and dry environments. Friction and adhesion measurements were taken using a Si@sub 3@N@sub 4@ tip and constant force mode in AFM/LFM. Friction force mapping provides insight into the localized change in friction caused by the application of hair care materials. Force-volume plots to study adhesion on the cuticle surface provide information about localization and change as well. A discussion is presented on these properties of hair as a function of ethnicity, wet and dry environments, and conditioning treatments.

SS-MoP35 A New @super 3@He Spin-Echo Spectrometer for Ultra-High Resolution Inelastic and Quasi-Elastic Helium Atom Scattering, *A.P. Jardine,* University of Cambridge, UK, U.K.*; P. Fouquet, S. Dworski, **G. Alexandrowicz**, H. Hedgeland, J. Ellis, A. Allison,* University of Cambridge, UK

Quasi-elastic helium atom scattering (QHAS) is a unique tool for studying surface dynamics on atomic length and picosecond time scales@footnote 1@. Conventional QHAS experiments, using time-of-flight methods, have limited resolution due to the velocity spread in the probing helium beam and can only investigate exceptionally fast processes. The recently established technique of @super 3@He spin-echo@footnote 2@@footnote 3@ is not limited by the velocity spread and can be used to study surface diffusion events over much greater time scales. The method is based on manipulating the precession of the nuclear spin in a polarised beam of @super 3@He atoms. Any energy change at the surface is seen as a change in the final polarisation of the beam. The key difficulty in applying the SE techniques to surface studies is in achieving a fully spin-polarised beam at sufficiently high energy (~8 meV) for a sufficient range of momentum transfers to be probed, to allow full k-space mapping of surface processes. We have have recently completed commissioning of a unique @super 3@He Spin-Echo apparatus, which operates at such beam energies. We show that the instrument increases the range of measurable time scales by three orders of magnitude. The main features of the apparatus are described, and we illustrate its the scope of application with recent experimental data, not only for surface diffusion, but also for the measurement of surface vibrations and helium-surface potentials. The results have unprecedented accuracy. @FootnoteText@ @footnote 1@ A. P. Jardine, J. Ellis and W. Allison, J. Phys. Condens. Matter 14, 6173 (2002)@footnote 2@ M. DeKieviet et. al. Phys. Rev. Lett. 75, 1919 (1995)@footnote 3@ M. DeKieviet et al. Surf. Sci. 377-379, 1112 (1997).

SS-MoP36 Electrochemical Micromachining with Ultrashort Voltage Pulses: Modeling and Simulation*, **J. Kenney,** G.S. Hwang,* The University of Texas at Austin

Recent results using electrochemical systems show promise for the areas of three-dimensional etching, high aspect ratio etching, and controlled deposition. These methods employ a â?otoolâ? electrode held in close proximity (~1 micron) to a reactive â?osubstrateâ? electrode in the presence of an electrolyte and utilize ultrashort (~50 ns) voltage pulses to modify the substrate surface selectively. The shape and feature resolution of synthesized structures would be determined by a complex combination of i) charging and discharging of electrochemical double layers at electrode surfaces, ii) electrochemical reactions on the electrodes, and iii) transport of molecules to the electrode surface. Experiments may provide many clues to the fundamental behaviors of electrochemical systems, but their interpretations often remain controversial due largely to difficulties in direct measurement. While current experimental techniques are still limited to providing complementary real space information, the interplay between experiment and theory will contribute to uncovering intricate kinetic phenomena involved in the electrochemical micron-scale patterning. In this talk, we present our multiphysics computational model for electrochemical micromachining with ultrashort voltage pulses. This approach integrates i) a circuit model to describe charging and discharging of electrochemical double layers and electric field variation in electrolytes and ii) the level set method to simulate feature profile evolution during electrochemical etching. Our simulation results of transient current responses and etch profile evolution are qualitatively in excellent agreement with experimental observations. From our simulations, we find that the resolution of etched features is a strong function of the substrate double layer capacity which may be controlled by electrolyte concentration and pulse duration.

SS-MoP37 Measurement of Gibbs Free Energies of Surfaces in Vacuum, and their Use to Explain the Pressure Dependence of the Thickness of a Lead-Oxide Film*, L. Bouzidi,* ***A.J. Slavin,*** Trent University, Canada

A method has been developed, using a high-stability quartz-crystal microbalance (HS-QCM)@footnote 1@, for determining the difference between Gibbs free energies of different surface oxide phases in ultrahigh vacuum. This is the only technique capable of such measurements, to our knowledge. These measurements have been used to explain the dependence, on oxygen pressure, of the thickness of a lead-oxide film grown on a gold substrate. The HS-QCM has also been used to measure a Pb:O ratio of 1:1, suggesting PbO as the surface oxide. Only the surface Pb monolayer oxidizes at an O@sub 2@ pressure of 5 x 10@super -6@ torr, with 1 x 10@super -4@ torr required to oxidize a second layer. For large Pb deposits on Au only the top two layers are oxidized up to an oxygen pressure of 10@super -2@ torr, apparently due to kinetic limitations. These results are quite different from the oxidation of pure Pb. @FootnoteText@ @footnote 1@ L. Bouzidi, S.S. Narine, K.G. Stefanov and A. J. Slavin; Rev. Sci. Instrum. 74, 3039-3044 (2003). .

SS-MoP38 Chemical Binding of N-Containing Aromatic Molecules on Si Surfaces: Mechanistic Understanding of the Selectivity of Reaction Channels*, **F. Tao,*** Princeton University*; G.Q. Xu,* National University of Singapore, Singapore

Chemical binding of organic molecules on Si surfaces is an important approach for fabricating molecular architectures to develop Si-based molecular devices and biosensors. Our studies on attachment chemistry of pyrrole, N-methylpyrrole and pyridine demonstrate the diversity of reaction channels of aromatics on Si surfaces. Pyrrole dissociatively chemisorbs onto Si surfaces through breaking the N-H bond, forming a pyrrolyl ring. Due to the absence of the N-H bond, N-methylpyrrole covalently binds to Si surfaces via pericyclic reactions. The difference of chemisorption mechanism between pyrrole and N-methylpyrrole demonstrates a strategy of switching the reaction channel by introducing substituted group. Besides the pericyclic reaction, pyridine can chemically bond to Si surfaces with the formation of SiN dative bond. Compared to pyrrole and N-methylpyrrole, the ability of pyridine to form a dative bond results from higher electron density around the N atom. This is due to localization of the lone-pair electrons on the N-atom for pyridine, contrasted with participation in the aromatic conjugation for pyrrole and N-methylpyrrole.

Thin Films

Room Exhibit Hall B - Session TF-MoP

Poster Session

TF-MoP1 Effect of the Deposition Parameters on the Microstructure and Optical Properties of Yttria-stabilized Zirconia Thin Films Deposited by r.f. Reactive Magnetron Sputtering*, M.H. Shiao,* National Science Council, Taiwan*; **C.W. Peng**,* Kun Shan University of Technology, Taiwan*; C.Y. Su,* National Science Council, Taiwan*; C.C. Jiang,* Ming Hsin University of Science & Technology, Taiwan*; S.C. Chang,* Kun Shan University of Technology, Taiwan

Yttria-stabilized zirconia (YSZ) thin films were prepared on (100) Si and quartz substrates by r.f. reactive magnetron sputtering system. Different oxygen to Argon (O@sub 2@/Ar) flow rate ratios (0% and 2.5%) and working pressures (0.33 Pa to 0.8 Pa) were investigated in the substrate temperatures ranging from room temperature to 500°C. Microstructure and surface roughness (R@sub a@) were examined by X-ray diffraction (XRD) and atomic force microscopy. Optical properties such as refractive index, extinction coefficient and transmission spectrum were measured by spectroscopic ellipsometer and spectrometer. It was found that without oxygen flow rate and the working pressure controlled at 0.33 Pa, the process have the highest deposition rate (2.5 nm/min), the highest transmittance (92.65%) and the lowest surface roughness (2.5 Å) at the deposition temperature of 300 °C. The YSZ crystalline orientation gradually changes from (111) to (200) when the deposition temperature above 300°C. When the oxygen to Argon flow rate ratio was 2.5% and the working pressure controlled at 0.33 Pa, the surface roughness decreases with increasing deposition temperature. But it still has the highest deposition rate (1.52 nm/min) and the highest transmittance (92.35%) at the deposition temperature of 300°C. The phase changes from amorphous to crystalline above the deposition temperature of 300°C. The deposition rate, surface roughness and transmittance decreased with increasing working pressure when the oxygen to Argon flow rate ratio and deposition temperature were controlled at 0% and 300°C, respectively.

TF-MoP2 (CdTe)@sub 1-x@Al@sub x@ Thin Films Grown by RF Co-sputtering for Photovoltaic Applications@footnote 1@*, L.A. Estrada - Domínguez,* ESFM-IPN, México*; **M. Meléndez-Lira**,* Cinvestav-IPN, México, Mexico*; M. Becerril-Silva,* Cinvestav-IPN, México*; M. Zapata-Torres,* CICATA-IPN, México*; S.J. Jiménez-Sandoval,* Cinvestav-IPN, México

Solar cells based on the heterostructure CdS/CdTe have been under a continuous development and there are commercial devices available. However, still there are problems limiting the efficiency predicted theoretically. Between the limiting factors, we found the difference in crystal structure between de CdTe (cubic) and CdS(hexagonal) and the inherent production of defects at the CdS/CdTe interface. Besides the interface problems, there are some difficulties to doping CdTe as p-type . We have produced (CdTe)@sub 1-x@Al@sub x@ films by RF co-sputtering employing CdTe and Al targets under an Ar atmosphere. Al content was controlled by the RF power of the Al magnetron. An increase in the bandgap depending on the Al content was found and values up to 1.61 eV for 6% of Al content were obtained . The samples presented hexagonal structure with lattice parameters values depending on the Al content, as determined by EDX. Raman spectroscopy clearly shows the incorporation of aluminium into the CdTe lattice. We will present in this work the results of an electrical transport characterization obtained by the Van deer Paw resistivity method and Hall effect measurements. We have found that for some growth conditions we can produce low resistivity samples with p-type conductivity. The results of the electrical characterization will be correlated with studies of the spectral photoresponse, optical and structural characterization carried out on the (CdTe)@sub 1-x@Al@sub x@ films. We propose a (CdTe)@sub 1-x@Al@sub x@ film as a solution for some of the problems presented in photovoltaics devices based on the CdS/CdTe heteroestructure using it to replace the CdTe film. @FootnoteText@ @footnote 1@: work partially supported by CONACyT-México.

TF-MoP3 Tailored Stoichiometries of Silicon Carbonitride Thin Films Prepared by Combined RF Magnetron Sputtering and Ion Beam Synthesis*, **M. Bruns**, U. Geckle, V. Trouillet,* Forschungszentrum Karlsruhe GmbH, Germany*; M. Rudolphi, H. Baumann,* Universitaet Frankfurt /Main, Germany

There is great interest in the ternary system Si-C-N due to the expected attainability of materials combining the properties of silicon carbide and silicon nitride. Various precursor based techniques have been employed to synthezise silicon carbonitrides. Most of these efforts result in compounds of deficient nitrogen content and considerable hydrogen and oxygen impurities. In contrast, combined RF magnetron sputtering and ion implantation are suitable to achieve high-purity ternary phases with tailored stoichiometries. Si-C films with defined Si/C ratios can be obtained using co-sputter targets of different Si/C area ratios. In a subsequent step surface modification of these Si-C films by high fluence implantation of N ions results in suitable nitrogen concentrations. Severalfold N implantation at different energies enables us to synthesize films with homogeneous element depth-distribution up to the surface. In this work we focus on the most interesting tie lines C@sub 3@N@sub 4@ - Si@sub 3@N@sub 4@ and SiC - Si@sub 3@N@sub 4@. Implanting N ions into sputtered Si-C films enables us to achieve every stoichiometry within the Si-C-N phase diagram. However, the region of attainable stoichiometries is narrowed by formation of Si-C-N phases and N@sub 2@, respectively. For Si/C ratios @<=@1 the N content of 57.4 at.% required for the formation of Si-C-N compounds on the tie line C@sub 3@N@sub 4@ - Si@sub 3@N@sub 4@ cannot be reached by N implantation near RT. @paragraph@The chemical composition of the Si-C-N films was characterized by means of X-ray photoelectron spectroscopy. In addition, Auger electron spectroscopy, Fourier transform infrared spectroscopy, Raman spectroscopy, and Ellipsometry were used to achieve a comprehensive characterization. For quantification XPS and AES data were calibrated with absolute concentration values from non-Rutherford backscattering spectrometry. Resonant nuclear reaction analysis provides non-destructive depth profiles of @super 15@N.

TF-MoP4 Combinatorial Synthesis of Rare Earth-doped Yttrium Aluminum Garnet Thin Film Materials by Using rf Reactive Magnetron Sputtering*, **Y. Deng**, J.D. Fowlkes, P.D. Rack,* University of Tennessee

Yttrium aluminum garnet (YAG) is known to be good host material for rare-earth doped luminescent materials. The rare earth ion typically substitutes for the yttrium sites which have a D2 symmetry in the YAG. The emission spectrum depends on the dopant type. Gadolinium radiates in the ultra-violet region at a dominant wavelength of ~ 312 and 275nm due to intra-band 4f transitions, while cerium peaks from 500 to 650nm due to interband 4f-5d transitions. To investigate the luminescence characteristic of dopants, thin films of gadolinium-doped and cerium-doped yttrium aluminum garnet (YAG:Gd and YAG:Ce) have been deposited by rf reactive magnetron sputtering. The dopant concentration effect on the cathodoluminescent (CL) properties of the films has been studied. Optimized conditions have been achieved by using a combinatorial thin film synthesis technique. The structure and composition of the films have been characterized by scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS). The crystallinity of the films has been investigated by X-ray diffraction (XRD). The luminescence properties of the films will be correlated to the chemical and microstructural properties of the films.

TF-MoP5 Electrical Properties of Ni-Cr Thin Films Deposited by Co-Sputtering Method*, **G.-B. Park**,* Yuhan College, Korea*; P.-K. Shin, B.-J. Lee,* Inha University, Korea

For thin resistor films with low TCR (temperature coefficient of resistance) and high resistivity, we have prepared the thin films by co-sputtering method with pure Ni and Cr targets and studied the effect of the process parameters on the electrical properties. In sputtering process, DC/RF power and pressure are varied as controllable parameters. We have investigated the microstructure and measured the electrical properties. When the Ni/Cr ratios of the deposited thin films were 0.8â^¼1.5, the resistivity was 100â^¼120 µ @OMEGA@Â·ãŽ. Below a Ni/Cr ratio of 1.5 (above 40[wt%] of Cr), the TCR became negative. The TCR of the thin films decreased from â?"30 ppm/°C to â?"75 ppm/°C with increasing Cr content. It is suggested that the composition ratio and electrical properties of thin films can be controlled by variation of sputter process parameters.

TF-MoP6 Target Surface Oxide Layer Formed by Reactive Sputtering of Ti Target in Ar+O@sub 2@ Mixed Gas*, **Y. Abe**, K. Takamura, M. Kawamura, K. Sasaki,* Kitami Institute of Technology, Japan

Reactive sputtering is a useful method for preparing compound thin films by sputtering metal targets in active gas atmosphere. The surface state of the metal target changes with sputtering conditions and makes important effects on deposition rate, chemical composition of the thin films, and plasma state, however, quantitative studies on the surface state of the target were scarce. In this study, TiO@sub 2@ films were deposited by reactively sputtering a 2-inch diam. Ti target in a mixed gas of Ar and O@sub 2@ using a planar RF magnetron sputtering system. Ti model target, a 1 µmm-thick Ti film sputter-deposited on the surface of a Si wafer, was used as a sputtering target for an experiment on target oxidation. The thickness of the oxide-layer formed at the surface of the model target was measured by ellipsometry. Effects of oxygen flow ratio and RF power on the surface oxide-layer-thickness were studied. The oxide layer formed at the surface of the Ti model target was confirmed to be TiO@sub 2@. The measured oxide-layer-thickness increased with increasing oxygen flow ratio, however, the maximum oxide-layer-thickness formed by sputtering in 100% O@sub 2@ gas was only several nano meters. No appreciable dependence on RF power and the position at the surface of the target was observed. However, methods of target cooling influenced the surface-oxide-thickness, which indicates that the oxide-layer-thickness increases with increasing target temperature.

TF-MoP7 Water Absorption and Dielectric Changes in Crystalline Poly(vinylidene fluoride-trifluoroethylene) Copolymer Films*, **L.G. Rosa**, P.A. Jacobson,* University of Nebraska-Lincoln*; C.M. Othon,* University of Nebraska-LIncoln*; K.L. Kraemer, A.V. Sorokin, S. Ducharme, P.A. Dowben,* University of Nebraska-Lincoln

Crystalline Langmuir Blodgett Copolymer films of vinylidene fluoride with trifluoroethylene (70%:30% and 80%:20%) absorbs water. Water absorption is accompained by film swelling as indicated by an increase in lattice spacing, sometimes by as much as 5%. This water absorption, between 0°C and 40°C, is a result of intercalation or occupation of interstitial sites between the layers of the film, not just water molecules filling voids and deffects site alone. An increase in the film capacitance is observed, although the polymer chains retain all trans configuration of the ferroelectric phase.

TF-MoP8 Water-incorporation in Reactively Sputtered Carbon Nitride Coatings*, **B.L. French**, Z. Yang, B.C. Holloway,* College of William and Mary

Carbon nitride is a candidate material for tribological/passivating overcoat layers on magnetic recording media due to its low friction coefficient, thermal stability, and high hardness. However, carbon nitride coatings are susceptible to damage from water in humid environments, resulting in an increase in friction coefficients, permeation of water to the underlying coating or delamination if sufficient stress is induced. In the present study carbon nitride coatings were prepared by DC planar magnetron sputtering. The working gas composition and pressure were systematically varied to manipulate coating morphology and composition. After growth, the deposition chamber was back-filled with air at a relative-humidity of 35% while stress in the coating was monitored in real-time with a laser-based wafer-curvature measurement system. The stress evolution during these experiments will be used to understand mechanisms of water-interaction with the coating and discussed in the context of existing models of water incorporation in thin films.

TF-MoP9 Deposition of Thin Films on Inclined Surfaces Using Ionized PVD*, **M. Lattemann**, J. Alami, J. Böhlmark, U. Helmersson,* Linköping University, Sweden

Titanium thin films were deposited, using a highly ionized flux of deposition material, onto substrates mounted at different angles (@gamma@ = 0, 45, 70, 90, 135, and 180°) with respect to the sputtering source. The results show that dense films were obtained independent of film orientation. In comparison films grown with conventional d.c. magnetron sputtering showed films of low density for @gamma@= 90° and higher angles. The deposition rate decreased in both cases with increasing angle @gamma@, but less so for the ionized deposition flux. The deposition rate, 5 mm from the edge of the sample, was reduced to 66 and 25% at @gamma@ = 90° and @gamma@ = 180°, respectively, in the case of ionized flux. This can be compared with less than 30% for @gamma@ = 90° in case of the non-ionized flux. The ionized-PVD technique used was high power pulsed magnetron sputtering (HPPMS) that is estimated to give an ionization degree of up to 70%. By applying a negative substrate bias the metal ions were attracted to the substrate surface independently of the inclination angle. The energetic ionized deposition flux leads to an effective transfer of kinetic energy to the surface which is the reason for the densification of the films grown using HPPMS. Due to its ease of use, the HPPMS technique is believed to have prospect of becoming an important technique for deposition of, e.g., hard coatings and corrosion resisting coatings onto substrates of complex shapes.

TF-MoP10 TCO Thin Film Characteristics with Respect to Multi Layer Coatings between Plastic Substrate and ITO Layer*, **M.G. Kim**, H.S. Jeong, Y.W. Seo,* ITM Inc., Korea*; S.J. Kwon,* Kyungwon Univ., Korea

Recently organic electro luminescence displays(OELD) using a plastic substrate such as PET and PES are emerging as a strong new candidate for flat panel displays. In this study we made the buffer layer which is multi-layer coatings such as (DLC/SiO@sub 2@)@sub n@ between plastic substrate and transparent conducting oxide(TCO). To minimize the oxygen transmission and the water vapor transmission of the TCO coated substrate, we also designed the thicknesses of multi-layer for high visible transmittance using optical thin film software. The DLC is characterized by strong hardness, flatness and low gas permeability to moisture and oxygen. The unipolar pulse mode of the power supply(IBP1030, ITM, Inc.) was used on a graphite target, and the mixed gas were argon and methane. ITO was deposited on the buffer layer of the plastic substrate in a horizontal single ended in-line sputter system equipped with a pulsed dual magnetron sputter. To understand the properties of the ITO films deposited on the multi-layered buffer layer, we investigated the electrical resistivity, film structure, optical transmission, surface roughness, and gas permeability.

TF-MoP11 Photoluminescence Behaviors of Eu-doped Sr@sub 2@SiO@sub 4@ Thin Film Phosphors Deposited by Pulsed Laser Deposition*, **S.S. Yi**,* Silla University, Korea*; J.S. Bae, J.H. Jeong,* Pukyong National University, Korea*; J.H. Kim,* Dongeui University, Korea*; H. Park,* Yonsei University, Korea

Sr@sub 2@SiO@sub 4@:Eu thin film phosphors were deposited on Al@sub 2@O@sub 3@ (0001) substrates by pulsed laser deposition. The Sr@sub 2@SiO@sub 4@:Eu thin films were grown at the various substrate temperatures and the different oxygen pressures. The crystallinity and surface morphology of the films were investigated using X-ray diffraction and atomic force microscope, respectively. And the photoluminescence spectra were measured at room temperature using a luminescence spectrometer and excitation by a broadband incoherent ultraviolet light source with a dominant excitation wavelength of 254 nm. The crystallinity and surface morphology of the films were influenced by the deposition conditions. It was found that the luminescence of the Sr@sub 2@SiO@sub 4@:Eu films is highly dependent on the crystallinity and surface roughness of the films. The Eu-doped Sr@sub 2@SiO@sub 4@ film shows two emission bands of 577 and 625 nm.

TF-MoP12 Luminescence Characteristics of Eu-doped GdVO@sub 4@ Thin Films Grown by Pulsed Laser Deposition, *J.H. Jeong, **J.S. Bae**, B.K. Moon, H.J. Seo,* Pukyong National University, Korea*; S.S. Yi,* Silla University, Korea

GdVO@sub 4@:Eu@super 3+@ thin film phosphors were deposited on Al@sub 2@O@sub 3@ (0001) substrates by pulsed laser deposition. The films were grown at the various substrate temperatures and the different oxygen pressures. The crystallinity and surface morphology of the films were investigated using X-ray diffraction and atomic force microscope, respectively. And the photoluminescence spectra were measured at room temperature using a luminescence spectrometer and excitation by a broadband incoherent ultraviolet light source with a dominant excitation wavelength of 254 nm. The photoluminescence brightness data obtained from GdVO@sub 4@:Eu@super 3+@ films grown under optimized conditions have indicated that sapphire is a good substrate for the growth of high quality GdVO@sub 4@:Eu@super 3+@ thin film red phosphor. Due to a @super 5@D@sub 0@-@super 7@F@sub 2@ transition within europium, GdVO@sub 4@:Eu@super 3+@ shows red luminescence at 612 nm. The crystallinity and surface morphology of the films were influenced by the deposition conditions. It was found that the luminescence of the GdVO@sub 4@:Eu@super 3+@ films is highly dependent on the crystallinity and surface roughness of the films.

TF-MoP13 Preparation of Transparent and Conductive Multicomponent Zn-In-Sn Oxide Thin Films by Vacuum Arc Plasma Evaporation, *T. Minami, **S. Tsukada**, Y. Minamino, T. Miyata,* Kanazawa Institute of Technology, Japan

A newly developed vacuum arc plasma evaporation (VAPE) method has recently attracted much attention for its high rate deposition of low-resistivity transparent conducting oxide (TCO) thin films on large area substrates. TCO thin films such as Ga- or F-doped ZnO and ITO were prepared by the VAPE method with resistivities on the order of 10@super -4@@ohm@cm. In this paper, we describe the preparation of transparent and conductive multicomponent Zn-In-Sn oxide thin films. Multicomponent Zn-In-Sn oxide fragments prepared by sintering a mixture of ZnO, In@sub 2@O@sub 3@ and SnO@sub 2@ powders were used as the target. The film depositions were carried out under the following conditions: substrate, large area glass; substrate temperature, RT to 350°C; pressure, 0.08 to 1 Pa; Ar and O@sub 2@ gas flow rates, 20 and 0 to 20 sccm; and cathode plasma power, 3.5 to 10 kW. Highly transparent and conductive multicomponent TCO thin films could be prepared by varying the composition of ZnO-In@sub 2@O@sub 3@, In@sub 2@O@sub 3@-SnO@sub 2@ and ZnO-SnO@sub 2@ fragment targets. It was also found that the metal content in the deposited films was approximately equal to that of the target used. In addition, a deposition rate above 100 nm/min as well as uniform distributions of resistivity and thickness on the substrate surface were obtained. Resistivities of 10@super -4@ to 10@super -3@@ohm@cm and average transmittances above 85% in the visible range were obtained in the ZnO-In@sub 2@O@sub 3@, In@sub 2@O@sub 3@-SnO@sub 2@ and ZnO-SnO@sub 2@ thin films deposited by varying the composition (metal content). In conclusion, approximately the same electrical and optical properties that had been previously reported in multicomponent Zn-In-Sn oxide thin films prepared by magnetron sputtering have now also been obtained using the VAPE method.

TF-MoP14 Cathodic Vacuum Arc Deposition of MgO Thin Films on the Large Area Glass Substrate, ***L. Sunghun**, B. Sung-Kyu, K. Jong-Kuk, L. Gun-Hwan,* Korea Institute of Machinery and Materials, Korea

It is well known that MgO film is used as the protective layer in AC-plasma display panels(AC-PDPs). Until now, e-beam evaporation and reactive magnetron sputtering method has been mainly adopted to produce MgO protective layer over the electrodes on the front glass panel of the PDP. However, there are still some problems such as the higher sputtering rate at e-beam method and the lower growth rate at magnetron sputtering method. In this work, cathodic vacuum arc deposition was introduced to produce MgO films on large area glass substrate, which shows higher deposition rates and the large number of ionized particles and high ion energy. Magnesium was used as a source material and oxygen was introduced as a reactive gas. We have investigated (1) appropriate shape of target for large area coating with one rectangular Mg target with size of 300 x 90 mm and two circular Mg target with diameter of 75 mm and (2) stable arc operating condition such as arrangement of magnet, magnet field strength, arc current and introduction method of oxygen gas. It was concluded that the rectangular type is not suitable for large area coating because of it's low mass utilization efficiency and the stable arc operating condition for circular Mg target . A properly designed arc source module with multiple circular Mg target for MgO protective layer with good quality will be presented.

TF-MoP15 Chemical Mechanical Polishing Characteristics of SnO2 Thin Film for Gas Sensor Application, *Y.J. Seo,* DAEBUL University, South Korea*; **K.W. Choi**, W.S. Lee,* Chosun University, South Korea

The metal oxide has been increasing interest for application of advanced technology. Of these oxides, tin dioxide (SnO2) is of interest as an oxidation catalyst, gas sensor material, thin film micro-battery, and transparent conductor. For the application of tin oxide films, the controls of microstructure and surface morphology are required because the electrical and optical properties are dependent on them. Although there have been many reports on the formation or smoothing of hillocks of the thin films, those works still report lack consistency. Hillocks on thin film surfaces deteriorate light reflection, ultra large-scale integration (ULSI) pattern resolution, and device performance because they are dependent on surface morphology or roughness. A chemical mechanical polishing (CMP) process is a useful method for removing sub-microscale hillocks. Therefore, an understanding and control of microstructure and surface morphology are required for the advanced application of tin oxide films. In this paper, we report the CMP effects on the variation of morphology for tin oxide films prepared by RF sputtering system. In order to compare the polishing characteristics of SnO2 thin film, we investigated the CMP removal rate (RR) and within-wafer non-uniformity (WIWNU%), particle size distribution, and the microstructures of surface and cross-sectional layer by atomic force microscopy (AFM) analysis. This work was supported by a Korea Research Foundation grant (KRF-2002-005-D00011).

TF-MoP16 Defect Study Post the Tungsten Etch Back Process Step, *A. Sidhwa, **J. Zhang**, V. Varadarjan, C. Li, B. Le, G. Magsamen,* STMicroelectronics, Inc.

The tungsten etch back defects generated during the process with their relations to the wafer yield is studied in this paper. By understanding these defects the wafer yields can be improved and one can achieve maximum tool up time. For the tungsten etch-back (WEB) process, two kinds of processes are widely used in the manufacturing world: One is the pattern tungsten etch and the other is the blanket tungsten etch back. The tungsten etch back can either stop on titanium nitride (SOT) or stop on the oxide (SOX). This paper mainly focuses on the SOT process for the tungsten etch-back defects. During the Fluorine (F-) etch process; the F- ions from SF6 gas will etch the Tungsten (W) film at a faster rate as compared to the Titanium Nitride (TiN) film. Some of the TiN film will still be etched during the Tungsten Etch Back step. The by-products generated during the etch back step is in the form of titanium fluoride (TiFx). Sometimes the residual etch by-products are not completely pumped out of the chamber. The residual etch by-products may re-deposit on the chamber hardware which consists of the Aluminum and Aluminum Oxide parts. The residuals may react with chamber hardware generating TixAlx defects. In addition other defects are generated in the etch-back chamber. This paper describes a new kind of C, O, F, and Ti based particles observed after the tungsten etch back step at via levels. These defects were generated due to poor via cleaning process step which leaves the EKC residuals on the wafer. The residual defects on the wafers were hard to catch after via cleaning and after the Via Liner deposition process step. These residual defects would re-appear after the WEB process step. The mechanism of the formation of these defects is discussed in this paper along with method and implementation processes to reduce these defects.

TF-MoP17 Fabrication of Well-defined Cu Nanodots Based on an Electroless Plating using Diblock Copolymer Nanotemplate, ***S. Asakura**,* Waseda University, Japan*; A. Hozumi,* National Institute of Advanced Industrial Science and Technology, Japan*; K. Oda, A. Fuwa,* Waseda University, Japan

Increasing attention has recently been paid to the fabrication of copper (Cu) arrays of nm-scale in order to fabricate electronic devices. Among the several methods, the use of a diblock copolymer (DBC) thin film is promising, since an ordered nanostructure can be easily obtained by chemical or physical treatment. Here we report the fabrication of cylindrical Cu nanostructures onto a SiO@sub 2@/Si substrate through an electroless plating using a DBC thin film as a template. First, a polystyrene (PS, 70 wt.%)/Poly(methylmethacrylate) (PMMA, 30 wt.%) DBC was spin-coated on the SiO@sub 2@/Si surface from a 3 wt.% in toluene. After dried in air for 24 h, it was annealed in a vacuum oven for 24 h at a temperature of 170 °C. Due to this treatment, the PMMA component formed cylindrical domains in a PS matrix. Subsequently, the sample was photoirradiated with vacuum ultraviolet (VUV) light of 172 nm in wavelength for 15 min at 10@super 3@ Pa to decompose PMMA predominantly utilizing the difference in etching rate between PS and PMMA domains. Amino-terminated self-assembled monolayer (SAM) was absorbed onto the whole area of the substrate by chemical vapor deposition method using n-(6-aminohexyl)aminopropyltrimethoxysilane (AHAPS) as a precursor. After that, the substrate was sonicated in toluene and then rinsed with Milli-Q water. Finally, the substrate covered with the AHAPS-SAM was immersed into a PdCl@sub 2@ solution followed by treated in an electroless plating bath to deposit Cu selectively. Using an atomic force microscopy, we confirmed that the Cu deposition selectively occurred inside the cylindrical nanopores in which the PMMA domains were photochemically eliminated. This clearly indicates that Pd catalysts were tightly immobilized selectively on the nanopores even after sonication in toluene due to the existence of AHAPS-SAM. Cu nanodods with a diameter and a periodicity of about 20 and 30 nm were successfully fabricated on the 10 x 10 mm@super 2@ region.

TF-MoP19 Observation of Plastic Deformation in TIALCN/A-C Ceramic Nanocomposite Coating*, **J. Shieh,*** National Nano Device Laboratory, Taiwan*; M.-H. Hon,* National Cheng Kung University, Taiwan

Titanium aluminum nitride, a metastable refractory ceramic coating, is widely used for improving tribological properties of cutting tools due to the excellent hardness and oxidation resistance.@footnote 1@ However, brittleness is a great handicap for ceramics in their technological applications since dislocations cannot move rapidly to allow for plastic deformation. Thus we added amorphous carbon into the grain boundary of nanograins to improve the coating plasticity. Extensive plastic deformation of titanium aluminum carbonitride/amorphous nanocomposite coating at room temperature was observed in this study. Nanoindentation measurement showed that the coating hardness was 24.4 GPa with the plasticity of 57.6 percent. The critical load of 1.3 µm coating in scratch test was beyond 100 N. The depth of the 100 N scratch track identified by microstylus profilometer was 6.7 µm, while the thickness of the coating in the center of the scratch track observed by scanning electron microscopy was 0.4 µm, which is only about one third of that for the as-deposited coating. The amorphous carbon with sp@super 2@ hybrid and @pi@-bonding is proposed to account for this unique plasticity. @FootnoteText@ @footnote 1@ S. PalDey and S.C. Deevi, Mat. Sci. Eng. A 342, 58 (2003).

TF-MoP20 Strained Si n-channel Metal-oxide-semiconductor Transistor on Relaxed SiGe Film with an Intermediate Si:C Layer*, **S.-W. Lee,*** National Tsing Hua University, Taiwan*; P.S. Chen,* Industrial Technology Research Institute, Taiwan, Republic of China*; Y.L. Chieh,* National Tsing Hua University, Taiwan*; M.-J. Tsai, C.W. Liu,* Industrial Technology Research Institute, Taiwan*; L.J. Chen,* National Tsing Hua University, Taiwan, Republic of China

An intermediate Si:C layer in the SiGe film, replacing the conventionally graded buffer layer, was used to form the high-quality relaxed SiGe substrate. With the 700-nm-thick SiGe overlayer, such a SiGe/Si:C/SiGe heterostructure has a threading dislocation density of 5.5x10@super5@ cm@super-2@ and a degree of strain relaxation of 98%. From the TEM observation, the numerous misfit dislocations were formed and confined at the top interface of SiGe/Si:C, maintaining a defect-free SiGe overlayer. Strained-Si n-channel metal-oxide-semiconductor transistors using this relaxed SiGe substrate were fabricated and their characteristics were examined. The effective mobility of the strained-Si device exhibits an enhancement of roughly 90% over that of Si control device at a given effective field. This work provides a simple method for the formation of strained Si layers.

TF-MoP21 Gas Barrier Properties of the Composite Films Consisting of SiO2 and SnO2*, **W.H. Koo**, S.M. Jeong, S.H. Choi, H.K. Baik,* Yonsei University, Korea*; S.M. Lee,* Kangwon National University, Korea*; S.J. Lee,* Kyungsung University, Korea

Composite thin films consisting of silicon oxide and tin oxide have been deposited on polycarbonate substrates as gas barrier films, using a thermal evaporation process in oxygen gas environment. Water vapor permeation through gas barrier films are significantly affected by the chemical interaction of water vapor with oxide films and the microstructure of the oxide films. The chemical interaction of water vapor with oxide films has been investigated by the refractive index from ellipsometry and OH group peak from x-ray photoelectron spectroscopy, and the microstructure of the composite oxide films characterized using x-ray diffraction, atomic force microscopy and transmission electron microscopy. As the tin oxide is added to the silicon oxide, the refractive index and OH group peak intensity of the composite films increase, and water vapor transmission rate through the composite oxide films shows the lower value than that through the sigle element oxide films such as tin oxide and silicon oxide. The results are discussed in terms of the chemical interaction with water vapor and microstructure of the oxide films.

TF-MoP22 Ultra High Resolution Tomographic Reconstruction Using Scanning Electron Microscope and Focused Ion Beam*, **R.K. Bansal**, R.V. Hull, J.M. Fitz-Gerald,* University of Virginia

The ever shrinking device dimensions in the semiconductor industry and the advent of nanotechnology has necessitated the developments of new characterization techniques which can work at smaller length scales with high precision. The present study aims at demonstrating a tomographic reconstruction technique capable of reproducing the morphology and chemical structure of a material with a sub-10nm resolution. This has been achieved by serial sectioning of the material using focused ion beam (FIB) and subsequent imaging using a high resolution field emission scanning electron microscope (FE SEM). This process was repeated to obtain a series of two dimensional cross sectional images. These images are then concatenated in the computer and interpolated into three dimensional space to asses and visualize the structure of the material. Multilayered structure of alternating 14nm thick Si-Ge/Si layers was reconstructed using linear interpolation of slices while a slightly more complex shape based interpolation routine was utilized to reconstruct @theta@' Al2Cu precipitates in Al matrix. As expected, the precipitates were found to be 10-20nm thick plates oriented along the orthogonal (100) directions even though this was not apparent from individual slices. High resolution alignment procedures were applied using FIB milled trenches and their profile was verified using cross sectional TEM. These trenches were also used to accurately predict the distance between individual slices. This is especially important as drift during milling in FIB often results in unequally spaced slices. Interpolation and visualization was performed using routines developed in MATLAB environment.

TF-MoP23 Deposition of Ti(C,N) AND Zr(C,N) Thin Films by Plasma Assisted MOCVD and In-Situ Plasma Diagnostics with Optical Emission Spectroscopy*, **J.-H. Boo**, S.W. Lee, Y.K. Cho, J.G. Han,* Sungkyunkwan University, South Korea

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

TF-MoP24 In-situ Characterization of HfO@sub 2@ and AlN Films on SiC*, **C.M. Tanner**, J. Choi, J.P. Chang,* University of California, Los Angeles

High dielectric constant materials are promising gate oxide materials for future generations of metal-oxide-semiconductor field effect transistor (MOSFETs). HfO@sub 2@ has a high dielectric constant and excellent thermal stability, indicating its suitability for high-power and high-temperature applications, especially when wide band gap semiconductors such as SiC are used as the substrate. Due to its close lattice matching with SiC, AlN is generally grown as a single crystalline layer on SiC and may provide an effective buffer layer between SiC and HfO@sub 2@. In addition, the AlN/SiC band offsets are quite symmetric, providing the needed barrier heights for an effective device operation. In this work, HfO@sub 2@ and AlN films were synthesized using atomic layer deposition (ALD) under high-vacuum conditions. Stacked HfO@sub 2@/AlN films were also grown on SiC in addition to the individual dielectric layers on SiC. The substrate temperature was controlled by infrared heating with a quartz tungsten halogen lamp. Hafnium tetra-tert-butoxide and oxygen were used to deposit HfO@sub 2@, while trimethylaluminum and ammonia were used to deposit AlN. Alternating pulses of chemicals were sequentially introduced into the reactor while film growth was monitored by in-situ reflection high-energy electron diffraction (RHEED) to study the surface structure. In-situ X-ray photoelectron spectroscopy (XPS) was used to study film composition and chemical bonding at the interface. The deposition kinetics of HfO_2 and AlN films were studied at various substrate temperatures and precursor doses. Film thickness and uniformity were determined by spectroscopic ellipsometry and confirmed with XPS. The microstructure of the interfaces of HfO_2/AlN/SiC stacked films was characterized using transmission electron microscopy (TEM).

**TF-MoP25 Conduction Anisotropy in Nanostructured Titanium Films*, D.W. Vick*, *M.J. Brett,* University of Alberta, Canada

Considerable control over the microstructure of evaporated thin films has been demonstrated using dynamic control of the vapour incident angle (α) and the azimuthal orientation of the substrate during the deposition process.[1] In the present study, advanced substrate motion is used to engineer the electrical properties of metallic films, and an attempt is made to relate measured electrical conductivity with observed film microstructure. Films with and without structural anisotropy will be included in the study. The regime of glancing angle deposition (GLAD) conditions ($\alpha \geq 80°$) is of particular interest to us. Under such conditions, significant voiding in the films results in a microstructure of isolated metallic islands whose mean size, shape, and separation are to some extent controllable. The experimental films consist of layers of Ti (nominal thickness 200 nm) deposited over barrier layers of SiO_2. Standard lithographic techniques are used to create arc-shaped tracks of 1 mm width, in a manner similar to that reported by Kuwahara and Hirota.[2] Metalization contacts and bonded wires are then added to the wafers, permitting measurement of electrical conductivity of the films and determination of the conduction anisotropy in the plane of the films. Preliminary results show that the ratio of conductivities along the two principal directions in the films can easily exceed a value of 7. Scanning electron microscope images that reveal the microstructure of the films will be presented together with conductivity measurements. Experimental results will be compared with the predictions of standard models of electrical conduction in discontinuous media. @FootnoteText@ [1] K. Robbie, J. C. Sit, and M. J. Brett, J. Vac. Sci. Technol. B 16, 1115 (1998). [2] K. Kuwahara and H. Hirota, Jap. J. Appl. Phys. 13, 1093 (1974).

**TF-MoP26 Monolayer Template Patterning of Ceramic Film on Flexible Plastic Substrate*, N. Shirahata*, *Y. Sakka,* National Institute of Materials Science, Japan*; A. Hozumi,* National Institute of Advanced Industrial Science and Technology, Japan

Microfabrication technique for metal oxide film on polymeric sheet has been demonstrated to develop flexible device technology. A polyimide (PI) sheet was employed as a polymeric substrate. Oxide nanoskin (ONS) interlayer (~ 2.1 nm) was formed onto the photooxidized PI (PIox) substrate by photochemical modification of the triethoxysilane layer, which was previously covered over the substrate through chemical vapor deposition process. 1H,1H,2H,2H-perfluorodecyltrimethoxysilane (FAS) molecule was used to prepare a microstructured chemical template for area-selective deposition of metal oxide films onto the predefined sites of the PIox surface. The film deposition was performed in aqueous solution of tin chloride based on under ambient air an environmental-friendly system. The ONS interlayer has played a key role through the microfabrication process. First, the ONS was indispensable to prepare a superior hydrophobic PI surface where highly ordered FAS molecules were densely formed. Second, the ONS enabled us to prepare an ideal FAS chemical template for the area-selective deposition of metal oxide film. Without the ONS interlayer, the reproducible results could not be obtained for the microfabrication. Additionally, on the ideal chemical template, thickness of the microfabricated films was well controllable in the ranging from nanoscale to microscale with keeping a perfect area-selectively. In this paper, the essential roles of ONS interlayer on both the preparation of high-quality chemical template and the reproducible microfabrication of metal oxide film, i.e., SnOx film, have been discussed in details.

**TF-MoP27 Comparison of the Agglomeration Behavior of Thin Metallic Films on SiO_2*, P.R. Gadkari*, *A.P. Warren, R.M. Todi, T. Cubano-Cruz, K.R. Coffey,* University of Central Florida

The preparation of continuous thin films of metals on insulating oxide surfaces is of interest to applications, such as semiconductor interconnections, as well as fundamental studies of transport in thin films. Noble and near-noble metals tend not to wet amorphous oxide surfaces and thus the equilibrium shape for the deposited metal is an isolated island on the substrate surface. For sufficiently thick films and/or reduced surface mobility, continuous metallic films can be formed by non-equilibrium processing. However, the geometry of such films is unstable, and upon annealing they can agglomerate and again form isolated islands on substrate surface. In this work we report the study of the formation of voids and agglomeration of initially continuous Ru, Pt, Cu and Au thin films deposited on amorphous thermally grown SiO_2 surfaces. Polycrystalline thin films having thicknesses in the range of 5nm to 100nm were UHV sputter deposited on thermally grown SiO_2 surfaces. The films were annealed at temperatures in the range of 150°C to 800°C in argon and argon+3% hydrogen gases. Scanning electron microscopy was used to investigate the agglomeration behavior and transmission electron microscopy was used to characterize the microstructure of the as-deposited and annealed films. The agglomeration of Ru and Cu films was observed to follow a grain boundary grooving process, whereas fractal growth of voids was observed in Pt and Au films. It is also observed that the tendency for agglomeration can be reduced by encapsulating the metal film with an oxide overlayer. Lastly, the variation of agglomeration with annealing temperature, gas ambient and film thickness is described.

**TF-MoP28 Effect of a Buffer Layer on the Photovoltaic Properties of AZO/Cu_2O Solar Cells*, T. Minami*, Kanazawa Institute of Technology, Japan*; H. Tanaka,* Gunze Limited, Japan*; T. Shimakawa, T. Miyata,* Kanazawa Institute of Technology, Japan*; H. Sato,* Gunze Limited, Japan

We have reported recently that high energy conversion efficiencies above 1% were obtained in Al-doped ZnO (AZO)/Cu_2O heterojunction solar cells fabricated by depositing transparent conducting AZO thin films on Cu_2O sheets. However, it is well known that a Cu metal thin film can easily be created at the interface by reducing the Cu_2O; therefore, the thin film deposition method and conditions are important considerations. In this paper, we describe the effect of a buffer layer and/or interface region on the photovoltaic properties of transparent conducting oxide (TCO)/Cu_2O solar cells fabricated with TCO thin films prepared by various deposition methods; we fabricated devices by depositing TCO films on Cu_2O sheets that had been exposed to various surface treatments or that had various thin films such as ZnO deposited as a buffer layer. The polycrystalline Cu_2O sheets (thickness of approximately 0.2 mm), prepared by heat treatment of Cu sheets (purity of 99.9%), functioned as the active layer as well as the substrate in the photovoltaic devices. Hall mobility in the resulting p-type semiconducting Cu_2O sheets was typically above 90 cm^2/Vs. The TCO and buffer layer thin films were deposited by pulsed laser deposition, d.c. or r.f. magnetron sputtering. The obtained dark current-voltage and photovoltaic properties in the devices were considerably affected by both the Cu_2O surface treatments and the introduced buffer layers. In addition, these properties were dependent on not only the method used in the TCO and buffer layer thin film depositions but also the deposition conditions. For example, the rectifying characteristics and the photovoltaic properties such as conversion efficiency and fill factor were found to improve in devices incorporating an undoped ZnO thin-film buffer layer. These obtained properties are mainly related to the work function and crystallinity of the deposited thin films as well as the crystallinity of the Cu_2O sheets.}

**TF-MoP29 Microstructural Evolution and Properties of the AlN Thin Films prepared under Different Processing Parameters*, C.-C. Wang*, National Chung Hsing University, Taiwan*; M.H. Shiao,* National Science Council, Taiwan*; C.-J. Lu, F.S. Shieu,* National Chung Hsing University, Taiwan

Polycrystalline aluminum nitride (AlN) thin films with wurtzite structure were deposited on silicon and glass substrates by an unbalanced magnetron (UBM) sputtering system equipped with a pulse dc power supply. Microstructure and chemistry of the AlN-coated substrates under different pulse power and deposition time were characterized by X-ray diffraction (XRD), field-emission scanning electron microscopy (FE-SEM), transmission electron microscopy (TEM), energy dispersive spectrometer (EDS) and atomic force microscopy (AFM). Optical transmission property of the AlN-coated glass was investigated by an UV/VIS spectrophotometer. XRD results show that the thin films exhibit enhanced (002) preferred orientation at higher pulse power and longer deposition time. It is also obtained that the AlN films have a columnar structure and that the size of the columns increases with the distance from the substrate and the deposition time, as revealed by FE-SEM and TEM. AFM analysis indicates that the surface roughness of the coatings increases with the pulse power and the deposition time. Furthermore, EDS analysis gives the chemical composition of the coatings as well as the percentage content of the elements. In addition, the energy band gap of the AlN films was evaluated to be 3.8-4.2 eV from the optical transmission spectra.

TF-MoP30 AFM and SNOM Characterization of Carboxylic Acid Terminated Silicon and Silicon Nitride Surfaces*, A. Cricenti,* National Research Council, Italy*; **R. Generosi**, M. Girasole,* CNR, Italy*; G. Margaritondo,* EPFL, Switzerland*; P. Thielen,* Naval Research Laboratory*; D. Vobornik,* EPFL, Switzerland*; J.S. Sanghera, I.D. Aggarwal,* Naval Research Laboratory*; N.H. Tolk, D.W. Piston,* Vanderbilt University*; A. Flamini, T. Prosperi, F. Cattaruzza, A. Mezzi, P. Perfetti, G. Ustione, A. Ustione,* CNR, Italy

Silicon and Silicon Nitride Surfaces have been successfully terminated with Carboxylic Acid monolayers and investigated by Atomic Force Microscopy (AFM) and Scanning Near-field Optical Microscopy (SNOM). On clean Si surface, AFM showed topographical variations of 0.3-0.4 nm while for the clean Si3N4 surface the corrugation was around 3-4 nm. After material deposition, the corrugation increased in both samples with a value in topography of 1-2 nm for Si and 5-6 nm for Si3N4. The space distribution of specific chemical species was obtained by taking SNOM reflectivity at several infrared wavelengths corresponding to stretch absorption bands of the material. The SNOM images showed a constant contribution in the local reflectance, suggesting that the two surfaces were uniformly covered.

TF-MoP31 Relationship of Microstructure and Discharge Characteristics of MgO Protecting Layer of AC-PDPs*, **S.Y. Park**, M.J. Lee, S.H. Moon, S.G. Kim, H.J. Kim,* Seoul National University, South Korea

MgO thin film is widely used as a protecting layer of the dielectric layer for alternating current plasma display panels(AC-PDPs) due to improvement of the panelâ?Ts discharge characteristics and lifetime. The discharge characteristics of AC-PDPs are critically dependent on the microstructure of MgO films; crystalline, surface morphology, and so on. We had focused on the relationship between microstructure of MgO protecting layer and discharge characteristics of AC-PDPs. MgO thin film was deposited with different E-beam evaporation source type; single crystal, melting, sintering, and powder. MgO thin film deposited with melting source had the highest density and peak intensity of (100) preferred orientation, but the film deposited with powder source had the lowest density, bimodal grain size distribution and oriented to (111) plane direction. It was due to the mobility of the adatom on the surface of growing MgO film. The variation of MgO source type led to change the various microstructures of MgO thin films in the same deposition condition, finally, it affected the discharge characteristics.

TF-MoP32 Thin Film Deposition of SiO@sub 2@ Using Electron-Beam Generated Plasmas*, **D. Leonhardt**, S.G. Walton,* Naval Research Laboratory*; C. Muratore,* ASEE/NRL Research Fellow*; R.A. Meger,* Naval Research Laboratory

The deposition of thin films of SiO@sub 2@ is an integral part of silicon and organic based electronics for flexible, large area applications such as flat panel displays, phased radar arrays and architectural lighting. The SiO@sub 2@ layer is the primary (high-k) dielectric of the device and 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 been using electron beam-generated plasmas for a wide variety of applications [1], including the etching of silicon and polymeric material. These plasmas offer tremendous scaling and uniformity capabilities and possess extremely low electron temperatures. The inherent low electron temperature results in low plasma fields and potentials, which in turn provides low energy (< 3 eV) ions to the substrate. Mixtures of TEOS and O@sub 2@ were used to grow SiO@sub 2@ films in modulated electron beam generated plasmas. The film electrical and optical properties with respect to gas mixtures, substrate type, temperature and ion energy will be presented. Fluxes to the substrate determined by mass spectrometry measurements will be correlated to these process variables and final film quality. Together with the previous etching work, electron beam generated plasmas may provide the critical dry processing necessary for flexible, large area electronics. Work supported by the Office of Naval Research. @FootnoteText@ @footnote 1@ See presentations by these authors at this and previous AVS symposia.

Applied Surface Science
Room 210A - Session AS-TuM

Electron Spectroscopies

Moderator: R. Haasch, University of Illinois, Urbana

8:20am **AS-TuM1 Light Induced Chemically Resolved Electrical Measurements (LICREM) in XPS: Anomalous Photoresponse of CdSe Nanoparticle Films***, **H. Cohen**, S. Sarkar, G. Hodes,* The Weizmann Institute of Science, Israel

A novel method, based on electrically and optically stimulated XPS, is applied to thin overlayers of CdSe nanoparticles. Negative differential resistance is observed in the dark chemically resolved electrical measurements (CREM)@super1@. The photoresponse under variable electrical conditions shows that the system can operate in two modes, differing in the direction of photocurrent. A phenomenological model is provided, explaining the anomalous photoresponse by means of competing charge trapping mechanisms, which allow real-time shaping of space charge and, hence, of the local electric fields. @FootnoteText@ @footnote 1@ H. Cohen, Condensed Matter Archive 031147, (Nov. 20, 2003).

8:40am **AS-TuM2 Validation of Information Gained from the XPS Survey Scan***, **J.E. Castle**, C. Lavie-Compin,* University of Surrey, UK

Members of the 34th IUVSTA workshop @footnote1@ reported an â?oimplementable protocol for the collection and analysis of a standard survey scan; allowing extraction of the maximum available informationâ?⍰. This information might then guide the next steps in sample analysis or might be sufficient in itself. Autonomous extraction of information required in corrosion science has been discussed @footnote2@. Here we compare data obtained from the survey scan with high resolution scans for four Cu/Ni alloys. They were examined: a) ion-etched ; b) carrying the air-formed oxide and contamination; c) after oxidation in air at 100ÂºC; and d) as c) with a brief ion-etch. The survey scan was used to determine key data including: a) testing for adventitious contamination by organic molecules @footnote3@; b) the thickness of the contamination layer; c) the apparent surface composition, corrected for the influence of contamination; d) the surface enrichment factor and enrichment rank; e) the principle chemical species in the surface, determined by the Auger parameter, and/or the presence of satellites @footnote4@; f) the thickness of the oxide, determined by peak fitting regions taken from the survey scan. The comparison enables the value of guidance given by the survey scan and the extent to which it is sufficient for purpose, to be assessed. @FootnoteText@ @footnote1@ J.E.Castle and C.J.Powell â?oReport on the 34th IUVSTA Workshop â?~XPS: from spectra to results â?" towards an expert systemâ?⍰ Surf.Interface Anal. 36 pp225 - 37 (2004) @footnote2@ J.E.Castle â?oModules for an XPS Expert System: Applications in Corrosion Scienceâ?⍰, QSA Symposium: AVS 50th Meeting, Baltimore 2003. @footnote3@ J.E.Castle and M.A.Bakerâ?oThe Feasibility of an XPS Expert System Demonstrated by A Rule Set for Carbon Contaminationâ?⍰ J. Elec Spec Related Phenomena, 105 pp245 - 256 (1999) @footnote4@ J.E.Castle â?~A Wizard Source of Expertise in XPSâ?T Surf.Interface Anal. 33 pp 196 - 202 (2002).

9:00am **AS-TuM3 Extensions of Photoelectron Spectroscopy to the Study of Nanoscale Systems***, **R.L. Opila**, K. Demirkan, A. Mathew,* University of Delaware **INVITED**

Photoelectron spectroscopy (PES) is a very powerful probe of elemental composition and structure at nanometer length scales. PES of core levels can identify which atoms are present, their relative concentrations, and their chemical bonding. PES of the valence levels yields more insight into the chemical bonding. This technique achieves its surface sensitivity from the charge on the photoelectron and its high probability of inelastic collisions. This complication provides both complications and opportunities. First, the photoelectrons are not collected as a linear function of depth, but approximately by an exponentially decreasing function of depth, where the decay length is given by an average of the emission depth distribution function. Collecting the emitted photoelectrons over several angles changes the sampled range of depths. Several algorithms have been proposed that permit the variation in intensity as a function of collection angle to be converted to elemental concentration as a function of depth. We will discuss a maximum entropy algorithm and show its application to study of high-k dielectrics as gate oxides for transistors. The charge on the photoelectrons also samples the local electronic charges that might be present. Through Coulombic interaction with these charges, their kinetic energy is shifted. It is possible to determine the amount of fixed charge present at a chemical interface by determining the relative shift between the photoelectrons emitted from overlayer and those from the substrate. Examples of interfacial charge, including high-k oxide/Si and Al2O3/Al, will be discussed.

9:40am **AS-TuM5 XPS Chemical Depth Profiling Using C@sub 60@ Ion Beams***, **N. Sanada**, A. Yamamoto, H. Iwai,* ULVAC-PHI, Inc., Japan*; J.F. Moulder,* Physical Electronics*; R. Oiwa, Y. Ohashi,* ULVAC-PHI, Inc., Japan

XPS is one of the most common analytical techniques which can be applied to the chemical analysis of a wide range of materials such as organic polymers, ceramics, metals and semiconductors. However, depth profiling with XPS requires sputtering with ion beams, which are well known to induce sample damage and have the constraint of sample chemical information being lost. Recently, we have applied a buckminsterfullerene (C@sub 60@) ion beam for depth profiling during XPS analysis[1]. A practical sputter rate of 2.4 nm / min. for SiO@sub 2@ was obtained with a sputtered area of 5 mm x 5 mm using a 5 kV C@sub 60@ ion beam. Extremely low sputtering degradation of organic polymers such as polytetrafluoroethylene[1], a polyester, a gelatin, and a latex [2] were observed under these conditions. In the meantime, the carbon contaminants derived from the C@sub 60@ ion beam varied under different sputter conditions. We studied the beam condition using a thermally oxidized SiO@sub 2@ film sample to minimize carbon residue determined by XPS. The quantities of carbon residue in the SiO@sub 2@ film reduced from 85 at% to 0.2 at% as the beam energies were modified from 2 keV to 30 keV. The incidence angle of the ion beam also affected the carbon residue in the film. XPS chemical depth profiling with C@sub 60@ sputtering applied to organic thin films will be discussed in this presentation. [1] N. Sanada et al., Surf. Interf. Anal., 36, 280 (2004). [2] N. Sanada et al., Extended Abstracts 51st Spring Meeting, 2004; Jpn. Soc. Appl. Phys. Rel. Soc. 29p-YD2.

10:00am **AS-TuM6 X-Ray Photoelectron Spectroscopy of Rubber Compounds: Temperature Dependence and Crosslink Distribution***, **G.E. Hammer**,* The Goodyear Tire & Rubber Company

Rubber compounds are complex mixtures of ingredients, including many mobile and volatile species. Exposure to the ultra high vacuum environment common to surface analytical instruments can therefore cause significant changes in a rubber surface and produce misleading and even erroneous results. In this work it has been shown that stable, representative x-ray photoelectron spectra could be obtained if the specimen was pre-cooled below a compound-dependent maximum temperature before exposure to the vacuum environment. Maximum temperatures were found to be -50°C and -70°C for two typical tire rubber compounds, a wire adhesion formulation and passenger tire tread, respectively. Effects of specimen preparation were further investigated. High resolution x-ray photoelectron spectra of specimens pre-cooled to -85°C and analyzed at -140°C indicated a correlation between the sulfur peak positions and the length of sulfur crosslinks in the rubber. Specifically, a linear relationship was found between sulfur 2p binding energy and the percentage of polysulfide crosslinks as determined by standard bulk solvent swelling analysis for three different rubber compounds based on two different polymers.

10:20am **AS-TuM7 Monte Carlo Simulations of Electron Backscattering from Surfaces in Scanning Auger Microscopy***, **C. Powell**,* NIST*; A. Jablonski,* Institute of Physical Chemistry, Poland

Monte Carlo (MC) simulations are useful for calculating signal intensities in AES because multiple-scattering events can be conveniently included. In this contribution, a new MC algorithm for AES is presented in which recent advances in knowledge of electron transport are incorporated. Differential cross sections for elastic scattering were obtained from a NIST database.@footnote 1@ The inelastic-scattering events were described by energy-loss functions derived from optical data, and "recommended" inelastic mean free paths for energies up to 10 keV were utilized.@footnote 2@ The empirical formula of Casnati et al.@footnote 3@ was used to describe inner-shell ionization cross sections. Particular care was taken in preparing the random number generators for simulation of the angular and energy distributions after elastic- and inelastic-scattering events because of numerous sharp features (e.g., deep minima) in the relevant probability distributions. We report new calculations of the backscattering factor (BF) for Auger transitions of Si, Cu, Ag, and Au as a function of primary energy, and find that the BF depends also on the Auger-electron emission angle. We investigated the radial distribution of emitted Auger electrons from a thin Cu film on Si and Au substrates. Due to the effects of electron backscattering, the radius of the analysis area depends considerably on the primary energy and the substrate, and can be much larger than the radius of the primary beam. We also examined the effects of backscattering on Auger line scans in the vicinity of the edge of a Cu film on Si and Au substrates. @FootnoteText@ @footnote 1@A. Jablonski, F. Salvat, and C. J. Powell, NIST Electron Elastic-Scattering Cross-Section Database, Version 3.1, SRD Database 64 (2003). @footnote 2@C. J. Powell and A. Jablonski, J. Phys. Chem. Ref. Data 28 (1999) 19. @footnote 3@E. Casnati, A. Tartari and C. Baraldi, J. Phys. B 15 (1982) 155.

10:40am **AS-TuM8 Round Robin Study of Evaluation of Electron Beam Damage of SiO2/Si in Auger Microprobe Analysis*, S. Tanuma,*** *T. Kimura,* National Institute for Materials Science (NIMS), Japan*; S. Hashimoto,* Kokankeisoku, Japan*; M. Inoue,* Setsunan University, Japan*; M. Suzuki,* ULVAC-PHI, Inc., Japan

Auger electron spectroscopy (AES) is routinely employed for characterization of wafers at various stages of device fabrication, for the identification of defects, and for process development. A major limitation of AES, however, is the fact that the incident electron beam can initiate unwanted chemical changes. While many investigations have been made on electron irradiation damage of silicon dioxide during analyses by Auger electron spectroscopy (AES), it is very complicated or tedious to determine the critical dose for such damage from intensity changes of the silicon L3VV Auger spectrum versus irradiation time. Then, we plan to make an accurate and quantitative method of the evaluation of surface damage on the specimen caused by the electron beam irradiation. We have made measurements of the Si L3VV spectrum on SiO2 (100nm)/Si and SiO2 (10nm)/Si specimens versus electron dose at 3, 5, 10 and 15 keV. The measurements were carried out for a wide range of the total irradiation dose: 0.001 - 150 C/cm2. We found that the peaks to background intensities of Si LVV metallic peaks are changed due to the increase of measurement time (or total electron dose). We have also developed an equation that represents the Si LVV metallic peak intensities as a function of total electron dose, based on the two-step decomposition model for SiO2. This method has two parameters that represent the EDCS of SiO2 and SiO, respectively. Form the curve fit of the proposed equation to the measured Si LVV metallic peak intensities, we can determine the critical dose of electrons for SiO2 decomposition quantitatively.

11:00am **AS-TuM9 Performance of a High throughput TOF-HREELS Analyzer*, Z. Yang,*** University of Maine*; R.H. Jackson,* Stillwater Scientific Instruments*; P.H. Kleban, B.G. Frederick,* University of Maine

Despite tremendous advances in monochromators, the efficiency of conventional analyzers in high resolution electron energy loss spectrometers (HREELS) is poor (~ 0.1%) due to the serial nature of the dispersive analyzer: only 1 out of typically 2000 energy channels can be measured at any one time. Pseudo-random binary sequence modulation is a method of multiplexing in the time domain to increase the throughput of the analyzer to 50%. We have combined PRBS modulation in an electron time-of-flight analyzer with maximum likelihood signal recovery methods to decrease data acquisition times from hours per spectrum to a few minutes, while maintaining resolution in the 2-4 meV range. We will present results from several samples that demonstrate the capabilities of the state-of-the-art time-of-flight TOF-HREELS instrument. Data measured on azimuthally oriented polytetrafluoroethylene (Teflon) films reproduce the complex spectral features and achieve resolution comparable to spectra measured with the conventional instrument. Results on the c(2x4) O/Pd(110) surface, in which the intensity of the oxygen-metal stretch relative to the elastic peak is < 0.1%, demonstrates the large dynamic range that has been achieved, again with resolution below 3 meV off the surface. Similar performance is obtained for CO/Pd(110), in good agreement with recently published spectra by Kato, et al.@footnote 1@. @FootnoteText@ @footnote 1@ Kato, H.; Okuyama, H.; Ichihara, S.; Kawai, M.; Yoshinobu, J. J. Chem Phys 2000, 112, 1925.

11:20am **AS-TuM10 Oxygen Environmental Electron Spectroscopy and Microscopy: A New Concept for Reducing Harmful Electron Beam Effects on Insulating Samples*, Y. Ji,*** *H. Guo,* Beijing University of Technology, China*; V. Kempter,* Technische Unviversität Clausthal, Germany

Charging phenomena occur on insulating surfaces in many types of surface analysis techniques. In the case of electron spectroscopy and microscopy using an electron beam as probe, the charging phenomena can seriously distort the spectra and images, even make the analysis impossible. In addition, the electron beam can change the surface composition through electron stimulated desorption (ESD) and electron stimulated adsorption (ESA). These effects on oxide samples in Auger electron spectroscopy analysis can be markedly reduced or eliminated in oxygen pressures @<=@ 6*10@super -@@super 6@ Pa. Using oxygen environment to reduce the surface charging-up is based on a novel concept: Reducing the charging effects through eliminating electron traps resulting from electron beam damage, specifically, the ESD of surface oxygen. This is a breakthrough in the understanding of the charging mechanism, as the existing methods for reducing charging-up are mostly based on considerations such as increasing the surface conductivity by coating a conducting layer, increasing the secondary electron yield by applying an additional low energy electron beam, neutralizing the negative surface charges by providing positive charges, increasing the bulk conductivity by sample heating, etc. The significance of this method is that it can also compensate the depletion of the surface oxygen due to ESD and eliminate the surface contamination from background adsorption; it is applicable to other analysis techniques such as scanning electron microscopy, electron probe microanalysis, electron diffraction, electron energy loss spectroscopy.

Biomaterial Interfaces
Room 210D - Session BI+NS-TuM
The Nano-Bio Interface

Moderators: G.J. Leggett, University of Sheffield, UK, M. Textor, ETH Zurich, Switzerland

8:20am **BI+NS-TuM1 Programmed Macromolecular Synthesis*, D.A. Tirrell,*** Caltech **INVITED**

We have developed three approaches to the synthesis of proteins and protein-like macromolecules containing novel amino acids. In the first approach, we replace every copy of one of the natural amino acids by an analogue, in effect building proteins from an altered set of twenty starting materials. This approach is most useful when one is interested in changing the overall physical properties of the protein, or in de novo design of protein-based biomaterials. A second method, which has also been implemented successfully by Schultz and coworkers, allows site-specific incorporation of a single copy of an amino acid analogue in response to a stop codon. Such methods are useful in probing protein structure and function. The third approach, developed most recently, uses mutant transfer RNAs to break the degeneracy of the genetic code, and offers the prospect of a protein chemistry based on a substantially expanded set of amino acid building blocks. This lecture will describe the most important elements of each of these strategies as well as some thoughts on the design of wholly artificial proteins with potential application in biotechnology and materials science.

9:00am **BI+NS-TuM3 The Art of Mechano-Transduction within the Extracellular Matrix*, V. Vogel,*** Swiss Federal Institute of Technology (ETH), Switzerland **INVITED**

While engineered matrices allow asking well defined questions of how cells interact and respond to their environment, it remains unclear whether a minimal set of cues exists by which synthetic matrices can be engineered that mimics biological matrices in their essential functions. Here we address how mechanical force can alter the conformation of extracellular matrix proteins and consequently regulate the display of the protein's functional states. The function of cells is tightly controlled by their interaction with the surrounding extracellular matrix to which they are coupled via the transmembrane integrins. Using intramolecular fluorescence resonance energy transfer (FRET), we studied the extent to which fibronectin is stretched and partially unfolded by the traction forces generated by fibroblasts in 2d and 3d matrices. We then derive structural models of the unfolding pathways of ECM proteins by computational techniques (steered molecular dynamics simulations), and gain insight how tension applied to extracellular matrix proteins affects the exposure of their molecular recognition sites. The consequences of our findings to the field of biomaterials and tissue engineering will be discussed. @FootnoteText@ V. Vogel, G. Baneyx, The tissue engineering puzzle: a molecular perspective, Annual Review Biomed. Eng., 5 (2003) 441-463. G. Baneyx, L. Baugh, V. Vogel, Co-existing conformations of fibronectin imaged in cell culture by fluorescence resonance energy transfer, Proc. Natl. Acad. Sci. USA, 98 (2001) 14464-14468. G. Baneyx, L. Baugh, V. Vogel, Fibronectin extension and unfolding within cell matrix fibrils controlled by cytoskeletal tension, Proc. Natl. Acad. Sci. USA, 99 (2002) 5139-5143. D. Craig, M. Gao, K. Schulten, V. Vogel, Structural insights how sequence variations tune the mechanical stability of fibronectin type III modules, Structure, 12 (2004) 21-30.

9:40am **BI+NS-TuM5 Capture and Release of Proteins on the Nanoscale by Surface-Confined Biomolecular Switches***, J. Hyun,* Seoul National University, Korea*; W.K. Lee, N. Nath, A. Chilkoti,* ***S. Zauscher,*** Duke University

In this paper we describe the fabrication and characterization of stimulus-responsive elastin-like polypeptide (ELP) nanostructures grafted onto ï⍰·-substituted thiolates that were patterned onto gold surfaces by dip-pen nanolithography (DPN). We exploited the hydrophilic-hydrophobic phase transition of ELP in response to a change in ionic strength as a switch in order to reversibly immobilize a thioredoxin-ELP fusion protein onto the ELP nanopattern above the lower critical solution temperature. We demonstrated the biological activity of the Trx-ELP nanoarray by binding an anti-thioredoxin monoclonal antibody. Furthermore, we showed that the resulting Trx-ELP/anti Trx-mAb complex could be released below the LCST. Our research demonstrates proof-of-principle that "smart," surface-confined biomolecular switches can be built at the nanoscale. Our method of fabricating switchable surfaces is attractive because it is entirely modular and generic, in that it only requires an ELP-modified or patterned surface and a protein that can be appended with an ELP tag. ELP synthesis is easily achieved through genetic engineering techniques. The nanoscale miniaturization of on-chip separation and the presentation and triggered release of the captured proteins made possible by this methodology should be integrable into nanoscale bioanalytical devices that are currently under development.

10:00am **BI+NS-TuM6 Micro- and Nanopatterns of DNA-Tagged Vesicles***,* ***B. Städler****, D. Falconnet,* Laboratory for Surface Science and Technology, Switzerland*; F Höök, I Pfeiffer,* Chalmers University of Technology, Sweden*; H Solak,* Paul Scherrer Institute, Switzerland*; J. Vörös,* Laboratory for Surface Science and Technology, Switzerland

A new approach for the creation of vesicular micro-and nanoarrays is presented based on a novel patterning approach termed Molecular Assembly Patterning by Lift-off (MAPL) in combination with the immobilization of DNA-tagged intact vesicles. This technique is shown to be a promising platform for future studies of enzyme and membrane protein activity in a controlled, native nanoenvironment. Fabrication of DNA microarrays by spotting is state-of-the-art today. This arraying technology, however, cannot be directly applied to membrane-based microarrays because the contact with the ambient environment damages the membranes. Our approach starts with conventional single stranded DNA arrays, which are subsequently converted into a membrane protein array by using phospholipidic vesicles tagged with the complementary DNAs. These functionalized vesicles specifically couple to the surface through hybridization of the DNA strands. The MAPL process was used to provide a surface with a background resistant to the nonspecific adsorption of vesicles and active spots (diameter between 1 and 200 µm) for the immobilization of the single stranded DNAs. The surface chemistry of the active spots and background consisted of biotinylated PEG and non-functionalized PEG, respectively. Complexes of biotin-terminated DNA and neutrAvidin, preformed in solution, were immobilized to the biotinylated, active spots. POPC vesicles tagged with complementary cholesterol-terminated DNA could then be specifically coupled to the surface through the hybridization of the DNA strands. Quartz crystal microbalance and optical waveguide technique were used to monitor in situ and optimize the multistep surface modification process. The micropatterns of DNA-tagged, fluorescently labeled vesicles were investigated by fluorescence microscopy. X-ray Interference Lithography was successfully used to downscale the patterning process to the nanometer scale in order to produce single vesicle arrays.

10:20am **BI+NS-TuM7 Label-Free Biosensor Based on the Surface Plasmon Resonance of Gold Nanoparticles***,* ***S.M. Marinakos****, N. Nath, A. Chilkoti,* Duke University

The optical properties of gold nanoparticles immobilized on a surface were used in a label-free biosensing scheme. The sensing modality is based on the change in the local refractive index associated with receptor-ligand binding at the particle surface which shifts the surface plasmon resonance (SPR) peak in the absorbance spectra of the nanoparticles. In previous work, we have shown that solid, spherical gold nanoparticles with a size in the range of 13-50 nm could be self-assembled on amine-functionalized glass. These chemisorbed nanoparticles were then functionalized with a biotin derivative. We showed that this scheme enabled single wavelength monitoring of streptavidin binding at the surface by single wavelength measurements of the change in intensity that was caused by binding of streptavidin at the nanoparticle-solution interface. In this study, we extend these measurements to anisotropic gold nanorods, in an effort to further improve the analytical sensitivity and detection limits of this label-free transmission optical sensor. Results will be presented that compare streptavidin-biotin binding with sensors fabricated from gold nanorods with previous results on spherical gold nanoparticles.

10:40am **BI+NS-TuM8 Activation of Integrin Function by Nanopatterned Adhesive Interfaces***, J.P. Spatz,* ***M. Arnold,*** University of Heidelberg, Germany **INVITED**

To study the function behind molecular arrangement of single integrins in cell adhesion, we designed a hexagonally close-packed rigid template of cell adhesive gold nano-dots coated with cyclic RGDfK peptide by lithographic means of diblock copolymer self-assembly. The diameter of the adhesive dots is = 73nm between the adhesive dots results in limited cell attachment and spreading and dramatically reduces the formation of focal adhesion and actin stress fibers. We attribute these cellular responses to restricted integrin clustering rather than insufficient number of ligand molecules in cell-matrix interface since "omicro-nanopatterned" substrates consisting of alternating fields with dense and no nano-dots support cell adhesion. We propose that the range between 58-73 nm is a universal length scale for integrin clustering and activation, since these properties are shared by a variety of cultured cells.

11:20am **BI+NS-TuM10 Lifetime of Biomolecules in Hybrid Nanodevices: The Aging Process of Motor Protein-based Molecular Shuttles***, H. Hess,* University of Washington*; C. Brunner,* ETH Zurich, Switzerland*; K.-H. Ernst,* EMPA Duebendorf, Switzerland*;* ***V. Vogel,*** University of Washington and ETH Zurich, Switzerland

Prolonging the lifetime of biomolecules in their functional states is critical for applications where biomolecules are integrated into synthetic materials or nanodevices. A simplified molecular shuttle system, which consists of fluorescently labeled microtubules propelled by kinesin motor proteins bound to the surface of a flow cell, served here as a model system for such a hybrid device. In this system, the functional decay can easily be assayed by utilizing optical microscopy to detect motility and disintegration of microtubules (MTs). We found that the lifetimes of these hybrid systems were mainly limited by the stability of MTs, rather than of kinesin. To determine the biocompatibility of polymers widely used in microfabrication, we assembled flow cells with glass bottom surfaces and covers fabricated from glass, poly(urethane) (PU), poly(methyl-metacrylate) (PMMA), poly(dimethylsiloxane) (PDMS), and ethylene-vinyl alcohol copolymer (EVOH). Without illumination, only PU had a substantial negative impact on MT stability, while PMMA, PDMS and EVOH showed stabilities comparable to glass. Under the influence of light, however, the MTs degraded rapidly on PDMS or PMMA. A similar effect was observed on glass if oxygen scavengers were not added to the medium. Strong bleaching of the fluorophores was again only found on the polymer substrates and photobleaching coincided with an accelerated depolymerization of the MTs. The presented data provide a benchmark for the lifetime of motor protein-based bionanodevices which utilize glass as the primary synthetic material, and test the impact of a variety of polymer materials on the longevity of microtubules, the most fragile biological structure in the device. This study demonstrates that our definition of biocompatibility evolves, as we progress towards architectures engineered on a molecular level, which integrate multimeric proteins and protein assemblies.

11:40am **BI+NS-TuM11 Analysis of Collision Events of Self-Propelled Biomolecular Shuttles Carrying Cargo***,* ***B.C. Bunker,*** *A.K. Boal, S.B. Rivera, G.D. Bachand,* Sandia National Laboratories

Collision events between cargo carrying biotinylated microtubules (MTs) laden with 0.56 mm diameter streptavidin coated polystyrene beads (SBs) while being transported across kinesin coated surfaces were observed. Six distinct actions resulted from such collisions: no interaction, SB transfer between MTs, one MT deforming as a result of the collision, co-joining of the two MTs through mutual attachment to the SB, the SB being dislodged from the MT, or one of the MTs being severed. Interactions were studied both as a function of percent biotin-tubulin used to prepare the MTs and temperature. While biotin percent was observed to have a negligible effect of the percent chance of the various outcomes, heating the system from 24ËsC to 30ËsC decreased the likelihood of a SB transfer event while increasing the rate of MT bending and dragging events. Two important factors are proposed to determine the outcome of these collisions: the geometry of the collision event and the nature of the binding site that the SB is originally attached to.

Electronic Materials and Processing
Room 304C - Session DI+PS-TuM

High-k Dielectrics: Growth and Processing

Moderator: A.A. Demkov, Motorola, Inc.

8:20am **DI+PS-TuM1 Inductively Coupled Remote Nitrogen Plasma Treatment of Hf Based Gate Dielectrics for Improved Interface Stability on Si(100)***, **T. Klein**,* University of Alabama **INVITED**

HfO@sub 2@ is a leading candidate for replacement of SiO@sub 2@ in CMOS field effect transistors. Past work has shown this material has a tendency to interdiffuse and react with the substrate forming a less-than-ideal abrupt interface. In this paper, HfO@sub 2@ thin film stability results for a remote plasma nitrification process is reported in which the Si substrate is exposed to a N@sub 2@/He plasma then annealed in vacuum before the gate oxide deposition process. The nitrided surface and subsequently deposited films were studied using ellipsometry and x-ray photoelectron spectroscopy before and after annealing treatments. This method is compared to other procedures for the addition of nitrogen developed in our laboratory including the plasma enhanced deposition of HfO@sub 2@ using N@sub 2@O and N@sub 2@ plasmas, and post deposition treatment of the films with a remote N@sub 2@ plasma. Nitrogen plasma treated substrates showed a nitride layer approximately 16 @Ao@ thick which was sufficient to prevent significant film/substrate interdiffusion and thickness growth for 2 min., 800@degree@C anneals in Ar.

9:00am **DI+PS-TuM3 In Situ Infrared Spectroscopy of High-k Dielectric Growth on Si (100)***, **R.T. Brewer**, M.-T. Ho, L. Ghoncharova,* Rutgers University*; M.P. Boleslawski,* Aldrich Chemical Co.*; T. Gustafsson, E. Garfunkel, Y.J. Chabal,* Rutgers University

We have used in situ, transmission infrared (IR) spectroscopy and ex-situ Medium Energy Ion Scattering (MEIS) to investigate the growth mechanisms of atomic layer deposition (ALD) of Al@sub 2@O@sub 3@ and HfO@sub 2@ on Si (100). The high-k materials were deposited by alternating exposures of organometallic precursors (trimethylaluminum for Al@sub 2@O@sub 3@ and tetrakis(ethylmethylamido)hafnium for HfO@sub 2@) and D@sub 2@O at ~300@super o@C. IR spectroscopy makes it possible to identify the adsorbed precursor products, the growth of the high-k films, and the formation of an interfacial layer, such as SiO@sub 2@. For ALD directly on hydrogen terminated Si (100) we observe the formation of interfacial SiO@sub 2@; moreover, several ALD exposure cycles are required before the high-k film can nucleate on the surface and begin to grow. Functionalizing the surface with a pretreatment of NH@sub 3@ results in high-k film growth from the first cycle exposure, and reduces the formation of interfacial SiO@sub 2@ by acting as a barrier and providing a nucleation layer for the high-k growth. In this talk, we will compare HfO@sub 2@ and Al@sub 2@O@sub 3@ growth.

9:20am **DI+PS-TuM4 DFT Study of the Initial ALD Reactions of Hf(N(CH3)2)4 on the SiO2 and Si-H Surfaces: Mechanism, Kinetics, Vibrational Spectra and Interface Structure***, J.G. Han, **C.B. Musgrave**,* Stanford University*; M.J. Kelley, G.N. Parsons,* North Carolina State University

Atomic layer deposition is ideally capable of depositing uniform thin films of materials one atomic layer at a time. In practice, the initial coverage of active sites on the starting substrate determines the initial growth rate, which is typically below the steady state growth rate. Furthermore, the initial reactions on the starting substrate are important in defining the atomic structure of the interface between the deposited film and the substrate. Because the electronic properties of advanced CMOS are highly sensitive to the electronic structure and thus the atomic structure of this interface, it is essential to gain control over the structure of the interface through the chemistry of the ALD process on the starting substrate. We have used ab initio electronic structure theory to calculate mechanisms leading to various interface structures for the reaction of a tetrakis(dimethylamido) hafnium precursor with Si-H and Si-OH terminated substrates and the resulting interface bonding. We also calculate the vibrational spectra for some possible surface species and compare these with those measured by FTIR. Our calculations show that the adsorbed metal precursor activates neighboring Si-H sites enabling subsequent reactions with water and the ALD metal precursor.

9:40am **DI+PS-TuM5 Development of Post Etching Process for Hf Based High-K Gate Dielectric***, **W.S. Hwang**, J.H. Chen, W.J. Yoo, D.S.H. Chan,* National University of Singapore, Singapore*; D.-L. Kwong,* University of Texas at Austin

For successful integration of high-K dielectrics into CMOS process, a technique to selectively remove high-K films and interfacial layers with minimum consumption of both Si substrate and shallow trench isolation SiO@sub 2@ needs to be developed. In this work, we studied the wet etching properties of Hf based high-K dielectrics using 1% HF (DHF) for HfO@sub 2@, HfSiO, and HfAlO deposited by atomic layer deposition or sputtering. Effects of anneal, plasma oxidation and nitridation are discussed. Results show that before anneal, all these films can be removed completely by DHF with etch rates higher than 12nm/min. After 700@super o@C anneal, etch rate of HfAlO does not change, whereas etch rate of HfSiO decreases ~ 50%, leaving ~ 1nm thick densified HfSiO interfacial layer unremoved. Furthermore, HfO@sub 2@ cannot be etched by DHF after anneal: after etching for 24 hours, no thickness change was observed. By applying the room temperature plasma oxidation treatment, HfSiO interfacial layer can be removed in 10s in DHF, but 3-6nm thick SiO@sub 2@ grows underneath HfSiO interfacial layer, resulting in significant recess into Si substrate. However, 2 nm thick HfO@sub 2@ can be removed in 10s in DHF without noticeable recess into Si substrate, by applying the room temperature plasma nitridation treatment. Surface analysis using X-ray photoelectron spectroscopy shows that Hf-N bonds are formed on the surface of HfO@sub 2@ after plasma nitridation. High etch rate of HfN of 1000Å/min in DHF can explain the increase of the etch rate by the incorporation of N. HfSiO interfacial layer was also removed in 10s after plasma nitridation. By the plasma nitridation aided DHF cleaning process, very little recess of both Si substrate and STI SiO@sub 2@ was achieved, and furthermore low contact NiSi sheet resistance of 4-5@ohm@/sq was achieved.

10:00am **DI+PS-TuM6 Plasma-Enhanced Atomic Layer Deposition for Compositionally Controlled Metal Oxide Thin Films***, **S.X. Lao**, R.M. Martin, 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 and higher processing yield. In this work, ZrO@sub 2@ and HfO@sub 2@ films were deposited using zirconium and hafnium tetra-tert butoxides as the metal precursors and oxygen radicals generated from oxygen plasma as the oxidant, introduced in alternating, cyclical sequence. 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. Optical emission spectroscopy (OES) was utilized to identify and quantify the gas phase atomic radicals. It was found that the OES intensity of oxygen radicals varies inversely with that of hydrogen radicals originating from the precursor. The presence of oxygen and hydrogen radicals in the gas phase resulted in the formation of surface hydroxyl groups, an important surface functional group for the chemisorption of precursors. As measured by the Fourier transform infrared spectroscopy (FTIR), the -OH integrated absorption intensities increased linearly with the number of deposition cycles and decreased upon annealing. Atomic force microscopy (AFM) analysis showed fairly smooth films with an RMS roughness of 1.7 Å after 5 deposition cycles. MOS capacitors were fabricated with the PEALD deposited films. The capacitance-voltage (C-V) and current-voltage (I-V) measurements showed that the PEALD HfO@sub 2@ films had the highest dielectric constant of 25 with an equivalent oxide thickness (EOT) of 12.5-15 Å. The leakage currents were several orders of magnitude less than that of SiO@sub 2@ films at the same EOT.

10:20am **DI+PS-TuM7 DFT Investigation of Initial HfO@sub 2@ Atomic Layer Deposition on Nitrided Silicon Surface***, **Y. Xu**, C.B. Musgrave,* Stanford University

The atomistic mechanism of the initial atomic layer deposition (ALD) reactions of hafnium oxide on a nitrided silicon surface was investigated using density functional theory (DFT). Reactions involving two different metal precursors are explored: Tetrakis-dimethylamido-hafnium (Hf[N(CH@sub 3@)@sub 2@]@sub 4@) and hafnium tetra chloride (HfCl@sub 4@). Hf[N(CH@sub 3@)@sub 2@]@sub 4@ forms no adsorbed complex on the nitrided Si substrate. The ALD ligand exchange reaction requires a barrier of 0.63eV and is exothermic by 0.22 eV. The adsorbed precursor state is not formed because the Hf atom of the precursor state has full s and d-shells and the amines are doubly bonded to Hf. Furthermore, the lone pair of nitrogen on the nitrided silicon surface is somewhat delocalized, reducing its ability to form dative bonds. Reaction between HfCl@sub 4@ and the nitrided silicon surface results in adsorbed HfCl@sub 4@ complex with an adsorption energy of 0.66 eV. The ligand exchange barrier is 1.33eV relative to the complex structure and the overall reaction is endothermic by 0.50 eV. Consequently, the alkylamide precursor is both kinetically and thermodynamically superior to HfCl@sub 4@ for the initial ALD reactions on the nitrided surface. We previously showed that for ALD of HfO@sub 2@, Hf[N(CH@sub 3@)@sub 2@]@sub 4@ appears to be a better choice than HfCl@sub 4@ both thermodynamically and kinetically. Thus Hf[N(CH@sub 3@)@sub 2@]@sub 4@ precursor performs better for both the initial reaction on the nitrided silicon surface and subsequent ALD of the HfO@sub 2@.

10:40am **DI+PS-TuM8 Oxygen Transport Properties in Hafnium Silicate Films***, D. Starodub,* ***L. Goncharova****, E. Garfunkel, T. Gustafsson,* Rutgers University*; G. Bersuker, B. Foran, P. Lysaght,* International Sematech

Developing an understanding of the kinetics and thermodynamics of film growth during fabrication of CMOS high-K gate stacks is thought to be critical in enabling control of interfacial layers, defects and other film properties. In this presentation we present new results on the oxygen transport mechanisms and kinetics in hafnium silicate films as a function of composition, structure and annealing conditions. The silicate films were grown on Si(001) substrates with and without nitride incorporation. To study oxygen transport, incorporation and interfacial growth, reoxidation of as grown and annealed films was performed in isotopically labeled oxygen-18. Oxygen isotopic distributions were then measured using high-resolution medium energy ion scattering. With a nitride layer present, the interface oxidation was minimized, and reaction with oxygen was limited to exchange with network oxygen in the silicate film. This exchange saturated with time and appeared to be enhanced after film recrystallization, perhaps due to an increase in grain boundaries. The films directly grown on H-terminated substrates exhibited additional oxygen incorporation at the interface with SiO@sub 2@ formation. This process increases with increasing film crystallinity, opening more permeable diffusive pathways via crystallite grain boundaries. We also explore PDA effects on oxygen permeability of the silicate films.

11:00am **DI+PS-TuM9 Investigation of the Roles of Oxygen Plasma and Solvent in the Pulsed-Liquid Injection PE-MOCVD Deposition of Y@sub2@O@sub3@ High-@kappa@ Materials in MIM Structures***,* ***C. Vallee****, C. Durand, M. Derivaz, M. Kahn, M. Bonvalot,* CNRS, France

CMOS scaling and Metal-insulator-Metal (MIM) capacitance density improvement will require use of new high-@kappa@ dielectric material in a near future. We have focused our work on the elaboration of Y2O3 thin films at low thermal budget (350°C) by pulsed-liquid injection Plasma Enhanced MOCVD for MIM capacitors (TiN-Y2O3-TiN). In this technique, dissolved Yttrium @beta@-diketonate Y(tmhd)@sub 3@ precursors (in cyclohexane and octane) are sequentially injected into an evaporator, with accurate reproducibility in the amount of precursors delivered to a low frequency (380 KHz) plasma chamber, where a O@sub 2@ plasma is applied to induce precursor decomposition and surface reactivity. The respective roles of oxygen plasma and solvent composition in the Y2O3 high-@kappa@ materials characteristics and interface properties have been investigated. The plasma is monitored by optical emission spectroscopy (OES) while films and interfaces are mainly characterized by X-rays Photoelectron Spectroscopy (XPS). Electrical characterizations are also performed in order to obtain capacitance density, voltage linearity and electrical breakdown properties. We have shown that a low plasma power and a high pressure limit carbon contamination while a high injection frequency limits interface reactions (as observed on SiO2/Si substrates). With this technique a capacitance density up to 6 fF/µm@super 2@ has been obtained. We have also investigated the effects of two solvents, cyclohexane and octane, in this study : it has been observed that deposition rate is strongly influenced by solvent nature. In addition, we also studied the effect of nitrogen plasma before, during and after deposition. Chemical bonding, concentration, and distribution of N in Y-oxide films after deposition and after high-temperature annealings are also characterized. The N concentration distribution in high-k dielectrics is likely to be an important factor to achieve optimal electrical performances.

11:20am **DI+PS-TuM10 UV Activated Surface Preparation of Silicon for High-k Dielectric Deposition***,* ***C.C. Finstad****, A.J. Muscat,* University of Arizona

High-k gate materials, such as HfO@sub 2@, are unstable on silicon, readily forming a low permittivity interfacial oxide when heated. A single layer of silicon nitride grown prior to gate dielectric deposition could serve as a diffusion barrier to prevent oxide formation. Moreover the SiN layer should promote nucleation of the dielectric film, thereby acting as both a barrier and a seed layer. A monolayer film of surface amine groups will be chemically similar to the hydrogen atoms of surface hydroxyl groups; therefore a pin-hole free monolayer of amine groups should simultaneously serve as both a diffusion barrier and a seed layer. This study aims to deposit a thin, continuous layer of surface amines at low temperatures (5.8 eV can photodissociate NH@sub 3@ molecules to yield NH@sub 2@ photofragments that react with H-terminated Si surfaces. With UV activation, N coverage increased with time and saturated at 1.7 ML. @FootnoteText@ @footnote 1@A. Nakajima et al., Appl. Phys. Lett. 80 (7), 1252 (2002).

11:40am **DI+PS-TuM11 Annealing of Hafnium Oxide Grown on Silicon by Atomic Layer Deposition: Changes in Interfacial Structure***, A. Deshpande,* University of Illinois at Chicago*; R. Inman,* ***G. Jursich****,* American Air Liquide*; C. Takoudis,* University of Illinois at Chicago

Thin films of hafnium oxide are deposited on Si(100) substrates by means of atomic layer deposition (ALD) using tetrakis(diethylamino)hafnium as the hafnium precursor and subsequently annealed at various temperatures (600-1000 C) under Ar atmosphere. The resulting composition and purity of the films are determined at different substrate temperatures using x-ray photoelectron and Fourier transform infrared (FTIR) spectroscopies. The chemical and physical structure of the film/interfacial regions are analyzed using a combination of Z-contrast imaging and electron energy loss spectroscopy (EELS) in the scanning transmission electron microscope. Depth profiling of film/interfacial regions were obtained using high-resolution angle resolved x-ray photoelectron spectroscopy (XPS). The pre-annealed films showed presence of a very thin silicon oxide at the film/substrate interface that originated from the residual surface oxide resulting from the wet chemical surface cleaning procedure used. Thus, no growth of interfacial region is observed from deposition alone. However, the post annealed films show increase in interfacial silicon oxide thickness coupled with formation of silicate-like structure as the annealing temperature is increased. This is evident from independent sets of data of FTIR spectroscopy and XPS. At the highest annealing temperature used (i.e., 1000 ÂºC), formation of silicide is observed at the interface. From these measurements detail information on the interfacial changes incurring from thermal annealing are obtained when there is a very thin layer of silicon oxide present on the silicon substrate. These results will be discussed in view of the intermediate SiO2 in terms of HfO2:SiO2 inter-diffusion and the formation of silicate-like structure.

Electronic Materials and Processing
Room 304B - Session EM-TuM

Contacts and Metallization

Moderator: S.E. Mohney, The Pennsylvania State University

8:40am **EM-TuM2 Near-Surface Defects and Schottky Barrier Formation at Au/ZnO(000-1) Interfaces***,* ***H.L. Mosbacker****, Y.M. Strzhemechny, P.E. Smith, B.D. White,* The Ohio State University*; D.C. Look,* Wright State University*; L.J. Brillson,* The Ohio State University

ZnO is rapidly emerging as a promising optoelectronic material, particularly for short wavelength light emitters. Key to such devices are an understanding and control of the metal-ZnO Schottky contact, yet clean interfaces and the role of extrinsic ZnO interface states in UHV barrier formation are relatively unexplored. We have used a combination of nanoscale depth-resolved electron-excited luminescence (NDREEL) spectroscopy, Auger electron spectroscopy (AES), atomic force microscopy (AFM), low energy electron diffraction (LEED), and current-voltage (I-V) measurements to correlate changes in Au/ZnO contacts with near-interface states and surface chemical structure. Eagle-Picher ZnO single crystals grown by chemical vapor transport and cleaned with organic solvents exhibit only minor contamination and a hexagonal LEED pattern. AFM revealed micro-pits known to render the metal/ZnO contacts ohmic. Subsequent exposure to a remote O/He plasma in a UHV-linked chamber resulted in a significant increase of rms surface roughness but an improved LEED pattern. AES surface stoichiometry improved after O/He plasma treatment with the O/Zn ratio increasing from ~ 0.55 to ~ 0.76. I-V of the in situ-evaporated Au/ZnO revealed dramatic change with plasma exposure: whereas the pre-plasma surface exhibited Ohmic behavior, the contact on the plasma-treated ZnO yielded a ~ 0.4 eV Schottky barrier with ~2 ideality factor. O plasma also significantly reduced 2.5 eV (i.e., green) NDREEL emission due to deep level (DL) traps by ~40% relative to the near band edge (NBE) emission both on and off the (semitransparent) Au contacts. In pre-plasma ZnO, the DL/NBE ratio was 40% higher at the free surface relative to that at ~ 90 nm deep. O plasma eliminated this near-surface increase. Further reduction occurred under the Au within < 20 nm of the interface. Our results are consistent with decrease in defect-assisted tunneling with plasma treatment vs. changes in Fermi level pinning.

9:00am **EM-TuM3 Investigation of the Sources of Variations in the Electrical Characteristics of Ohmic and Rectifying Contacts***, **L.M. Porter**, F.A. Mohammad, D.J. Ewing,* Carnegie Mellon University*; R.R. Ciechonski, M. Syväjärvi, R. Yakimova,* Linköping University, Sweden **INVITED**

Ohmic and rectifying contacts are widely known to yield significant variations in electrical properties, such as the contact resistance or Schottky barrier height. Importantly, these variations exist among contacts on the same substrate and therefore among contacts processed identically. In this study we have investigated more than one hundred ohmic and rectifying contacts on the wide band gap semiconductor, silicon carbide. The statistical variations in contact resistance, Schottky barrier height, etc. were quantitatively compared. As described below, the data indicate that multi-phase contacts and/or intrinsic or growth-related defects provide important sources of variability. We further show that control over these phenomena result in substantial improvements in the contact behavior. Ohmic contacts on p-type (1 x 10@super 19@ cm@super -3@) 4H-SiC were fabricated using both Pt and Pt-Si contacts and the conventional Al-Ti metallization. The Pt-Si contact layers were selected and processed such that single-phase PtSi contacts were produced, whereas the annealed Pt and Al-Ti contacts produced several phases. The single-phase PtSi contacts consistently yielded low contact resistances (4.9 x 10@super -5@ ohm-cm@super 2@) with a narrow distribution (standard deviation = 1.28 x 10@super -5@). Although the Al-Ti contacts yield comparable average contact resistance, the distributions in values for the multi-phase contacts were substantially higher. Nickel Schottky contacts were also investigated and showed a range of behaviors. For example, the barrier heights ranged from 0.88 - 1.36 eV and displayed an inverse correlation with the measured deep-level defect concentrations. The preliminary data also indicates that deep-level concentrations above ~5 x 10@super 13@ cm@super -3@ result in multiple-barrier characteristics in the forward I-V data.

9:40am **EM-TuM5 Simultaneous Formation of p- and n-type Ohmic Contacts to 4H-SiC using Ni/Ti/Al Contact Materials***, **S. Tsukimoto**, T. Sakai, M. Murakami,* Kyoto University, Japan

Both p- and n-type ohmic contacts are required for the future SiC power devices. Conventionally, these ohmic contacts are prepared using different materials and fabrication processes, because the current transport mechanisms for p- and n-type conductions are completely different. We succeeded to form simultaneously both p- and n-type ohmic contacts for 4H-SiC wide gap semiconductors using Ni/Ti/Al contact materials. The Ni/Ti/Al ohmic contacts were prepared by depositing sequentially Ni(20 nm), Ti(50 nm), and Al(50 nm) layers onto the p- and n-type SiC substrates which were doped with Al at 4.5x10@super 18@cm@super -3@ and with N at 1.4x10@super 19@cm@super -3@, respectively, and subsequently annealing at temperatures ranging form 600 °C to 1000 °C in an ultra high vacuum. The Ni/Ti/Al contacts showed ohmic behavior for both the p- and n-type SiC substrates after annealing at 800 °C. The specific contact resistances of these contacts for p- and n-type SiC were measured to be about 2x10@super -3@ @ohm@-cm@super 2@ and 3x10@super -4@ @ohm@-cm@super 2@, respectively. Based on interfacial microstructure analyzed by XRD measurements and cross-sectional TEM/HRTEM observations, the formation mechanism of the p/n-type Ni/Ti/Al ohmic contacts will be discussed.

10:00am **EM-TuM6 Fabrication, Processing and Specific Contact Resistance Measurements of Contacts to Semiconductor Nanowires***, **S. Dey**, Y. Wang, K.-K. Lew, T.S. Mayer, J.M. Redwing, S.E. Mohney,* The Pennsylvania State University

Ohmic contacts to semiconductor nanowires will be an essential component of many novel nanoscale electronic devices. In this presentation, we discuss the selection of metallizations and annealing conditions to lower the resistance of ohmic contacts to silicon nanowires, and we describe a method for measuring the specific contact resistance (or contact resistivity) of these contacts. To compare contact metallizations and processing conditions, silicon nanowires have been aligned using field-assisted assembly, and contacts have been fabricated using aluminum, palladium and titanium/gold metallizations. Aluminum and palladium contacts to p-type silicon nanowires have shown a reduction in contact resistance upon annealing. To then extract the specific contact resistance (or contact resistivity), equations have been developed that treat the metal/semiconductor nanowire contact as a transmission line, leading to the development of equations analogous to those used for describing contacts to semiconductor thin films using the transmission line model (TLM). The modified or nanowire TLM equations can be applied to several different metal/semiconductor nanowire test structures, and the advantages and disadvantages of the various geometries for testing the contacts are discussed. Finally, we provide the results of measurements in which we apply the nanowire TLM equations to a convenient test structure.

10:20am **EM-TuM7 CMOS Metal Gate Implementation***, **C. Cabral, Jr.**, V. Narayanan, J. Kedzierski, M. Copel, C. Lavoie, J.L. Jordan-Sweet, E.P. Gusev,* IBM T.J. Watson Research Center*; J.M.E. Harper,* University of New Hampshire **INVITED**

As scaling of CMOS transistors continues, for improved performance and manufacturing density, the leakage current through the thinner oxynitride dielectrics is becoming prohibitively large. Replacing the polycrystalline silicon in the gate with a metal is an approach, which leads to a decrease in the electrical thickness of the gate without having to decrease the physical dielectric thickness. The elimination of the poly-Si depletion region thus improves performance without substantially degrading leakage current. There are several integration schemes for implementing metal gates. There is a conventional approach for which the metal-dielectric combination must withstand high temperature dopant activation anneals, a gate last approach which limits the temperature to that used for the interconnect levels and a process by which the poly-Si of the gate is consumed in a reaction to form a metal silicide. Replacing the poly-Si in the gate typically requires a dual metal approach; a metal with a pFET workfunction and a second with an nFET workfunction. In this work a variety of metallic materials with workfunctions spanning the Si bandgap are characterized to determine the most appropriate integration approach for each based on the thermal stability of the metal-dielectric. In situ x-ray diffraction, optical scattering and resistance analysis, conducted at the Brookhaven National Laboratory, were used to determine when a metal-dielectric combination undergoes thermal degradation during annealing. It was found that some materials undergo reactions with the dielectric, others were unstable due to agglomeration, several binary compounds undergo dissociation and materials such as W, Re, Rh, Ir, TaN and TaSiN are very stable. The fully silicided metal gate integration approach will also be discussed. It will be demonstrated that the workfunction for NiSi can be modulated by the addition of implanted species into the poly-Si gate before silicide formation or by alloying the Ni.

11:00am **EM-TuM9 Physical and Electrical Properties of Mo@sub X@ N@sub Y@ and Mo@sub X@ Si@sub Y@ N@sub Z@ as Gate Electrode Materials for MOS Devices.***, R.M. Wallace, **P. Zhao**, P. Sivasubramani, I.S. Jeon,* University of Texas at Dallas*; J. Lee, J.Y. Kim,* Kookmin University, Korea*; M. Kim, B.E. Gnade,* University of Texas at Dallas

Continued CMOS scaling requires high-k dielectrics and advanced metal gate electrodes in the gate stack. The work function of Mo has been reported to be controlled with N@super +@ implantation.@footnote 1@. The use of amorphous ternary M-Si-N (M=Ta, Mo, W) as a diffusion barrier for Al or Cu metallization has been previously studied,@footnote 2 and 3@ and TaSi@sub X@ N@sub Y@ as a metal gate electrode candidate has been recently reported.@footnote 4@. In this study, the work function and thermal stability of Mo(N) and MoSi(N) deposited by reactive sputtering with different N@sub 2@/Ar ratios and with different nitrogen implantation doses were investigated. The defects and trapped charges in the interface were also analyzed using CV and IV measurements at different temperatures. XPS, XRD, RBS, TEM, CV and IV results will be presented. Our results indicate that Mo(N) and MoSi(N) are potential CMOS gate candidates. This work is supported by the Texas Advanced Technology Program.} $Footnotes {@footnote 1@ Rushkar Ranade, Hideki Takeuchi, Tsu-jae King and Chenming Hu, Electrochemical and Solid-State letters, 4 (11) G85-G87 (2001). @footnote 2@ J. S. Reid, E. Kolawa, R. P. Ruiz and M.-A. Nicolet, Thin Solid Film, 236, 319 (1993). @footnote 3@ J. S. Reid, E. Kolawa, R. P. Ruiz and M.-A. Nicolet, F. Cardone, D. Gupta and R. P. Ruiz, Journal of Applied physics, 79, 1109 (1996). @footnote 4@ You-Seok

Suh, Greg P. Heuss, Jae-Hoon Lee, and Veena Misra, IEEE Electron Device Letters, 24, 439 (2003).

11:20am **EM-TuM10 Influence of Interactions Between Ta-N Films and Low Dielectric Constant Materials on the Stability of Copper Interconnection***, C.-C. Chang,* National Cheng Kung University, Taiwan, Taiwan*; S.-K. JangJian,* Taiwan Semiconductor Manufacturing Company, Taiwan*; **J.-S. Chen,*** National Cheng Kung University, Taiwan

Low dielectric constant (low-k) materials integration with copper metallization has been adopted widely in integrated circuits. In this work, properties of copper layers in the Cu/Ta-N/Ta/low-k materials/ structures were explored, where Ta-N layers are as-deposited amorphous TaN@sub x@ (x~0.5) or polycrystalline TaN films and low-k materials include fluorinated silicate glass (FSG) and organosilicate glass (OSG), respectively. The samples in the Cu/Ta-N/Ta/low-k materials structures were annealed in vacuum at 400°C for 30 minutes or an hour. Thermal interactions between Cu and Ta-N films or Ta-N layers and low-k materials were investigated by using sheet resistance measurement, X-ray diffraction, scanning electron microscopy, X-ray photoelectron spectrometry, and transmission electron microscopy. As the thickness of Ta-N films decreases from 50 nm to 10 nm, the preferred orientation of (111)@sub Cu@ will be improved significantly in the Cu/TaN@sub x@ systems after annealing. On the other hand, as the thickness of the Ta-N films decreases to 5 nm, surface morphologies of these as-deposited and annealed copper layers are different obviously from the others with thicker Ta-N barriers. It is attributed to the interfacial reactions between the Ta-N layers and low-k materials and the properties of the ultra-thin Ta-N films itself. All of these effects would be discussed in this study.

11:40am **EM-TuM11 Low Resistivity Germanides***, **S. Gaudet,*** Ecole Polytechnique de Montreal, Canada*; C. Lavoie,* IBM T.J. Watson Research Center*; C. Detavernier,* University of Ghent, Belgium*; P. Desjardins,* Ecole Polytechnique de Montreal, Canada

In microelectronics, because of the availability of high dielectric constant material for gate oxide, CMOS devices can now be built on pure Ge substrates in order to take advantage of the higher carrier mobility of this semiconductor. While literature is readily available on possible contacts to SiGe devices, contacts to pure Ge are much less documented. We performed a systematic study of the reaction of metals with Ge substrates to identify appropriate contact materials. Thin films of 20 different metals (Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W, Mn, Re, Fe, Ru, Co, Rh, Ir, Ni, Pd, Pt, Cu) were deposited on amorphous Ge, Poly-Ge and Ge (100). Metal-Ge reactions were measured in situ during annealing using time resolved XRD, light scattering and resistance measurements. Among possible candidates for direct contact to Ge, two interesting monogermanides, NiGe and PdGe, form at low temperature and exhibit low resistance for a wide range of temperatures.

Magnetic Interfaces and Nanostructures
Room 304A - Session MI-TuM

Spintronics

Moderator: C.J. Palmstrøm, University of Minnesota

8:20am **MI-TuM1 Semiconductor Spintronics: From Basic Physics towards Spin Devices***, **M. Oestreich**, D. Hägele, J. Rudolph, S. Döhrmann, R. Winkler,* Universität Hannover, Germany*; H.M. Gibbs, G. Khitrova,* University of Arizona*; D. Schuh, M. Bichler,* Technische Universität München, Germany*; W. Stolz,* Universität Marburg, Germany **INVITED**

The electron spin in semiconductors has become a focus of intense research in the context of spintronic devices. A prime condition for the development of potential applications is the understanding of the spin decoherence, i.e. the loss of spin memory. In the first part of this talk we present the spin dynamics in (110) GaAs quantum wells at high temperatures and put forward a new spin dephasing mechanism that ultimately limits the high temperature spin dephasing times in GaAs quantum wells.@footnote 1@ In the second part of the talk we demonstrate the reduction of the threshold of semiconductor lasers by injection of spin polarized electrons, compare high and low temperature operation, and discuss problems and prospects of these spintronic devices.@footnote 2@. @FootnoteText@ @footnote 1@ S. Döhrmann et al., "Anomalous spin dephasing in (110) GaAs quantum wells: anisotropy and intersubband effects", cond-mat 0403052.@footnote 2@ J. Rudolph et al., "Laser threshold reduction in a spintronic device", Appl. Phys. Lett. 82, 4516 (2003).

9:00am **MI-TuM3 Characterization of Thin Film MnGa/GaAs(001) Heterostructures***, **J.L. Hilton**, B.D. Schultz, S. McKernan, C.J. Palmstrøm,* University of Minnesota

MnGa thin films are desirable for use as ferromagnetic contacts in spintronic devices because they can be grown epitaxially on GaAs with perpendicular magnetization@footnote 1@. The interface between the ferromagnetic contact and the semiconductor has a significant influence on the spin injection efficiency of spintronic devices. It has been shown previously that elemental Mn is not stable on GaAs and that it reacts to form an interfacial region composed of Mn@sub 2@As and MnGa@footnote 2@, suggesting that MnGa may be stable in contact with GaAs. However, bulk material studies suggest that Mn@sub 2@As and elemental Ga are the two stable phases in contact with GaAs@footnote 3@. To address this discrepancy, a number of MnGa/GaAs heterostructures were grown by MBE and subsequently annealed either in-situ or ex-situ for different times and temperatures. X-ray diffraction of MnGa/GaAs samples following growth shows peaks corresponding to both MnGa(001) planes and the GaAs substrate. Following post-growth anneals at 400°C for 1 hr, peaks corresponding to (001) planes of the Mn@sub 2@As-like crystal structure are observed. Rutherford backscattering spectrometry shows only minor compositional changes upon annealing, indicating that any reactions are confined to the interfacial region. These results will be combined with results from in-situ RHEED, LEED, STM, and XPS, and ex-situ RBS channeling and TEM to characterize the growth and interfacial properties of epitaxial MnGa/GaAs heterostructures. Supported by ONR, DARPA, NSF, and AFOSR. @FootnoteText@ @footnote 1@M. Tanaka et al., Appl. Phys. Lett. 62, 1565 (1993).@footnote 2@J. L. Hilton et al., Appl. Phys. Lett. 84, 3145 (2004).@footnote 3@P. Kordos et al., Solid State Electron 18, 223 (1975).

9:20am **MI-TuM4 Co@sub 2@MnGe/Ga@sub 1-x@Al@sub x@As Heterostructures: Growth, Characterization and Spin Injection***, **X.Y. Dong**, C. Adelmann, J. Strand, X. Lou, S. McKernan, J.Q. Xie, B.D. Schultz,* University of Minnesota*; A.K. Petford-Long,* University of Oxford*; P.A. Crowell, C.J. Palmström,* University of Minnesota

A number of ferromagnetic Heusler alloys of the type MMnX ("half" Heusler) and M@sub 2@MnX ("full" Heusler) have been predicted to be half-metallic @super 1@. The ability to grow Co@sub 2@MnGe epitaxially on GaAs, the predicted half-metallicity and the high Curie temperature, make it an ideal candidate for a spin injecting contact. Co@sub 2@MnGe epitaxial films were grown by molecular beam epitaxy (MBE) on Ga@sub 1-x@Al@sub x@As (001) surfaces prepared in a separate MBE-growth chamber and transferred in ultra high vacuum (<10@super -10@ torr) to the Heusler alloy growth MBE chamber. In-situ RHEED, ex-situ XRD and TEM demonstrate the epitaxial single crystallinity of the films. In-plane VSM measurements showed that the Co@sub 2@MnGe films have a 1000 emu/cm@super 3@ saturation magnetization at room temperature and a 8 Oe coercivity. A SQUID magnetometer was used to measure the out of plane magnetization, which was found to saturate around 1 Tesla. In order to measure the spin injection, tunneling Schottky barrier contact spin-LED structures were fabricated from MBE-grown p-Ga@sub 0.9@Al@sub 0.1@As/GaAs(100Å)/n-Ga@sub 0.9@Al@sub 0.1@As/Co@sub 2@MnGe/Al heterostructures. The 70Å thick Co@sub 2@MnGe Schottky barrier injector was grown at 175°C and the 25Å thick Al capping layer used to prevent oxidation during exposure to air was grown at 0°C. The epitaxial heterostructures were processed into LED devices and the devices were operated with the Schottky contact under reverse bias and the p-i-n LED under forward bias. Electroluminescence was collected along the sample normal. The circular polarization of the observed electroluminescence was 14% indicating a spin injection efficiency of 14% at 2K. To our knowledge, this is the first time demonstration of spin-injection from a Heusler alloy into a semiconductor. @FootnoteText@ @footnote 1@ S. Fujii, S. Sugimura, S. Ishida, and S. Asano., J. Phys.:Condens. Matter 2, 8583 (1990).

9:40am **MI-TuM5 Determination of the Influence of the Interfacial Formation and the Semiconductor Doping Profiles on the Spin Injection from Fe@sub x@Co@sub 1-x@ Contacts into Ga@sub x@Al@sub 1-x@As***, **C. Adelmann**, X.Y. Dong, B.D. Schultz, C.J. Palmstrøm, J. Strand, X. Lou, P.A. Crowell,* University of Minnesota*; S. Park, M.R. Fitzsimmons,* Los Alamos National Laboratory

Spin injection from ferromagnetic contacts into semiconductor structures is a crucial part in spintronic devices operating at room temperature. Recently, it has been shown that spin injection is possible from Fe into GaAs by tunneling through a reverse-biased Schottky contact into an light emitting diode@footnote 1@. The dependence of spin injection on the inter-face doping level and drift layer doping was studied. Efficient spin injection was only obtained in a narrow interface doping window between 3E18 and 5E18 cm@super -3@. The optimum drift layer doping was found to be about 1E16 cm@super -3@. The spin detection efficiency was also found to depend on the p-layer. The carrier transport as a function of doping level will be discussed. The effect of growth temperature and annealing on the spin injection was also investigated. Low temperature annealing was found to increase the electroluminescence polarization. However, at high annealing temperatures, no spin injection was observed suggesting reactions between GaAs and the metal contact. The observed changes in electroluminescence polarization were found to correlate with the changes in the interfacial magnetic properties for Fe@sub 0.5@Co@sub 0.5@/GaAs heterostructures determined from polarized neutron reflectivity. Optimized devices were found to lead to >10% spin injection at room temperature. This work was supported by the DARPA SPINS program, ONR, and the University of Minnesota NSF-MRSEC program. @FootnoteText@ @footnote 1@ A.T. Hanbicki et al., Appl. Phys. Lett. 80, 1240 (2002).

10:00am **MI-TuM6 Growth and Magnetic Properties of Group-IV Dilute Magnetic Semiconductors***, **Y.F. Chiang**, R.K. Kawakami,* University of California, Riverside

The synthesis of magnetically-doped semiconductors is important for electronics based on spin. We utilize molecular beam epitaxy (MBE) to incorporate magnetic dopants such as Mn and Co into Ge and Si semiconductor thin films. The structural properties of the samples are characterized by in situ reflection high energy electron diffraction (RHEED), x-ray diffraction, and transmission electron microscopy (TEM). Substrate temperatures during growth are monitored by a transferable thermocouple to ensure accurate thermometry for low-temperature growth (0-250Â° C). Magnetic hysteresis loops are measured by superconducting quantum interference device magnetometry (SQUID) and magneto-optic Kerr effect (MOKE) over a large temperature range (5K â?" 300K) in order to determine the Curie temperature, magnetic anisotropy, and remanence. The dependence of magnetic properties on the magnetic dopant concentration and the growth temperature will be discussed.

10:20am **MI-TuM7 Universal Scaling of Magnetoconductance in Magnetic Nanoconstrictions@footnote *@***, **S.-H. Chung**,* University of Maryland, College Park, Argonne National Laboratory **INVITED**

Large magnetoresistance in ferromagnetic transition metals, half-metallic oxides and magnetic semiconductors connected by nanoconstrictions has recently been observed by several research groups. In this work, we present new results that magnetoconductance in nanometer size constrictions has a universal scaling behavior [1]. The results were obtained for half-metallic ferromagnets formed by nanoconstrictions of CrO@sub 2@-CrO@sub 2@ and CrO@sub 2@-Ni. Analysis of the magnetoconductance versus scaled conductance data for all materials known to exhibits so-called ballistic magnetoresistance suggests that the magnetoconductance of nanoconstrictions follows universal scaling. If the maximum magnetoconductance is normalized to unity and the conductance is scaled to the resistivity of the material, then all data points from the current experiment and others in the literature fall into a universal curve that is independent of the constriction material and the transport mechanism. The results agree with a theory that takes into account the enhancement of spin scattering within a magnetic domain wall in nanoconstriction. The adiabatic spin transport increases as the width of the domain wall increases with the size of nanoconstrictions. This analysis suggests that the large magnetoresistance in the nanoconstrictions of materials even in different conductance regimes may have the same mechanism of spin-ballistic transport through magnetic nanoconstrictions. [1] S.-H. Chung, M. Munoz, N. Garcia, W. F. Egelhoff, and R. D. Gomez, Physical Review Letters vol. 89, 287203 (2002). @FootnoteText@ @footnote *@ Supported by the University of Maryland, College Park, NSF and MRSEC, by the Spanish DGICyT, and by the DOE, BES under contract W-31-109-ENG-38.@footnote **@ In collaboration with N. Garcia, M. Munoz, W. F. Egelhoff, H. Pandana, and R. D. Gomez .

11:00am **MI-TuM9 Spin-Transfer Torque in a Single Ferromagnetic Layer***, **Y. Ji**,* Argonne National Lab*; T.Y. Chen, C.L. Chien,* Johns Hopkins University*; M.D. Stiles,* National Institute of Standards and Technology **INVITED**

When a spin polarized current passes through a ferromagnet, spin angular momentum can be transferred between the conduction electrons and the magnetization of the ferromagnet. As a result, a torque is imparted on the magnetization, which will be realigned toward the polarization direction of the conduction electrons, an effect called â?ospin-transfer torqueâ?�. Previously most theories and experiments explore F/N/F trilayer or F/N multilayer structures, where F denotes a ferromagnet and N denotes a nonmagnetic metal. In low magnetic fields, the trilayers hysteretically switch between parallel and anti-parallel states, as the current is swept between polarities with a current perpendicular to plane (CPP) geometry. In high magnetic fields, reversible dV/dI peaks are observed for only one polarity of the current, and previously interpreted as the onset of spin-wave excitations. The multilayer or trilayer structures have been generally presumed indispensable, since non-collinear magnetizations between a polarizing layer and a receiving layer are required to generate spin torques, and the GMR effect is essential in detecting magnetization reversals. In this work, spin-transfer torque effects in a single ferromagnetic layer are demonstrated, using current injection through a point-contact. Differential resistance peaks are observed in high magnetic fields. The current values corresponding to the peak positions linearly depend on the external field. Hysteretic current-induced switching is observed in low magnetic fields. Systematic variations between low field and high field regions have been investigated and the implications will be discussed. The first author's work was done as a Ph.D. student in Johns Hopkins, supported by NSF DMR00-80031 and DMR97-32763. His current work at Argonne is supported by U.S. DOE BES-MS W-31-109-ENG-38.

11:40am **MI-TuM11 Magneto-Resistance in Epitaxial Nano-Contacts for Spintronic Device Applications***, **D. Pearson**,* University of Toledo*; R.A. Lukaszew,* University of Toledo, US

Ballistic magnetoresistance (BMR) research has shown surprising MR effects in electrodeposited Ni nano-contacts at room temperature and low magnetic field@footnote 1@. A large BMR effect may arise from non-adiabatic spin scattering across very narrow (atomic scale) magnetic domain walls (DW) trapped at nano-contacts@footnote 2@. Kent el al@footnote 3@ have studied MR in epitaxial microstructures and found small intrinisc DW related effects only on highly anisotropic films. We have studied nano-contacts in various other epitaxial films. The idea behind our scheme is that epitaxial ferromagnetic thin films may favor non adiabatic spin transport provided that the nano-contact is small enough as predicted by Bruno. We used a similar geometry to that utilized by Chopra and Garcia@footnote 1@,@footnote 4@. The combined shape and magnetocrystalline anisotropies provide the required two states for the magnetization at each side of the constriction. Our results indicate that domain walls do play a role in the magnetoresistance of these nano-bridges. Micromagnetic simulations where carried out on the Ni nanocontacts using OOMMF. We will present our work on epitaxial Ni, FeN and CrO@sub 2@ nano-contacts. FeN exhibits enhanced magnetic moment and is an attractive candidate for write-heads. CrO@sub 2@ is a half metal with 100 percent polarization and therefore of fundamental interest in these studies. @FootnoteText@ @footnote 1@ S. Z. Hua and B. D. Chopra, Phys. Rev. B. 67, 060401(R), 2003.@footnote 2@ P. Bruno, Phys. Rev. Lett. 83, 2425 (1999).@footnote 3@ Kent, et al., J. Phys: Condens. Matter 13 (2001) R461.@footnote 4@ N. Garcia, M. Munioz, V. V. Osipov, E. V. Ponizovskaya, G. G. Quian, I.G. Saveliev and Y.-W. Zhao, J. Magn. Magn. Mater. 240, 92 (2002).

MEMS and NEMS
Room 213C - Session MN-TuM
MEMS and NEMS: Enabling Tools for Scientific Research

Moderator: A.V. Sumant, University of Wisconsin at Madison

8:20am **MN-TuM1 C-MEMS/NEMS: A Novel Technology for Graphite, Ni, and Si Nanoscale Material Formation***, **M. Madou**, C. Wang, R. Zaouk, K. Malladi, L. Taherabadi,* University of California at Irvine **INVITED**

Carbon microelectromechanical systems (C-MEMS) and carbon nanoelectromechanical system (C-NEMS) have received much attention because of the many potential applications. BioMEMS applications include: DNA arrays, glucose sensors, microbatteries and biofuel cells. Microfabrication of carbon structures using current processing technology, including focused ion beam (FIB) and reactive ion etching (RIE), is time consuming and expensive. Low feature resolution, and poor repeatability of the carbon composition as well as widely varying properties of the resulting devices limits the use of screen printing of commercial carbon inks for C-MEMS. Our newly developed C-MEMS microfabrication technique is based on the pyrolysis of photo patterned resists. Using a suitable catalyst, graphite nanofibers and Ni nanowires were formed. Unlike conventional CVD methods for growing nanotubes in which a gaseous carbon source, such as CH4, is commonly used, we use photoresist as carbon source. Furthermore, Si nanowires were successfully grown without photoresist patterns and a modified solid-liquid-solid (SLS) mechanism was used to explain our results.

9:00am **MN-TuM3 Durability Studies of MEMS/NEMS Materials/Coatings at High Sliding Velocities (upto 10 mm/s) Using a Modified AFM*, N.S. Tambe*,** *B. Bhushan,* The Ohio State University

Most micro/nanoelectromechanical (MEMS/NEMS) devices and components operate at very high sliding velocities (of the order of tens of mm/s to few m/s). Micro/nanoscale tribology and mechanics of these devices is crucial for evaluating reliability and failure issues. Atomic force microscopy (AFM) studies to investigate potential materials/coatings for these devices have been rendered inadequate due to inherent limitations on the highest sliding velocities achievable with commercial AFMs. We have developed a new technique to study nanotribological properties at high sliding velocities (upto 10 mm/s) by modifying the commercial AFM setup with a customized closed loop piezo stage for mounting samples. Durability of various materials/coatings used for MEMS/NEMS applications such as silicon, diamondlike carbon (DLC), polydimethylsiloxane (PDMS), polymethylmethacrylate (PMMA), self assembled monolayer of hexadecanethiol (HDT) and perfluropolyether Z-DOL are studied at various normal loads and sliding velocities ranging between 1 µm/s and 10 mm/s. The effect of different sliding materials on the interface wear is studied by using three different AFM tips, viz. Si, Si@sub 3@N@sub 4@ and diamond. The tip wear is monitored by measuring the tip radii. The primary wear mechanisms for the different samples at high velocities are deformation of the contacting asperities due to impacts as in the case of single crystal silicon; phase transformation from amorphous to low shear strength graphite as found for DLC; localized melting due to high frictional energy dissipation as found for PDMS and PMMA; and substrate wear as found for HDT and Z-DOL. An analytical model is presented to explain wear mechanisms and different wear regimes at high sliding velocities.

9:20am **MN-TuM4 Chemical Control of Micromechanical Resonators: The Role of Surface Chemistry*, J.A. Henry*,** *Y. Wang, D. Sengupta, M.A. Hines,* Cornell University

The development of high-performance micromechanical resonators would enable advances in many technologies; however, many researchers have noted that the quality factor, or Q, of micromechanical resonators decreases with decreasing resonator size (i.e. increasing resonator frequency.) We have previously shown that the rate of mechanical energy dissipation, which is inversely proportional to Q, in MHz-range micromechanical silicon resonators is strongly affected by the chemical state of the resonator surface. In this presentation, we will present functionalized silicon resonators that have higher performance than the H-terminated resonators -- the previously demonstrated "best termination." Additionally, these functionalized resonators are relatively stable; little degradation is seen after a week in 100% humidity air. The implications of these results on the mechanism of surface-chemistry-induced mechanical energy dissipation will be discussed.

9:40am **MN-TuM5 Tribological and Wear Studies of ALD and SILAR Coatings for MEMS Devices*, C. Nistorica*,** *J.-F. Liu, I. Gory, G.D. Skidmore,* Zyvex Corporation*; F.M. Mantiziba, B.E. Gnade,* University of Texas at Dallas*; J. Kim,* Kookmin University, Korea

This paper describes a study of the static friction and wear of coated microelectromechanical systems (MEMS) using thermally actuated friction micro-devices. In order to characterize static friction and wear, a tribological deep reactive ion etched (DRIE) silicon test microstructure is developed. Reproducibility of the data is proved by testing multiple devices in parallel. Conformal coatings consisting of 10 nm thick atomic layer deposited (ALD) TiO@sub 2@ or ZrO@sub 2@ and successive ionic layer adsorption and reaction (SILAR) deposited MoS@sub 2@ or ZrO@sub 2@ films are applied on the MEMS silicon test devices. The effect of film roughness, velocity as well as the effect of humidity on friction and wear is studied by exposing the coated MEMS devices to a relative humidity varying between 5% and 100%. The coatings were found to behave differently, ZrO@sub 2@ and MoS@sub 2@ decreasing the coefficient of friction by 40% compared to uncoated devices, while TiO@sub 2@ presented a decrease in the coefficient of friction only at higher humidity. The wear data for the ALD coated devices, quantified from the point of view of debris creation and stability of the friction coefficient, indicate much improvement over native oxide coated silicon devices, while the SILAR coatings showed high wear.

10:00am **MN-TuM6 MEMS-based Force-Detected Nuclear Magnetic Resonance Spectrometer*, T. George*,** *K. Son, C. Lee, N.V. Myung, E.R. Urgiles,* Jet Propulsion Laboratory*; L.A. Madsen, G.M. Leskowitz, R.A. Elgammal, D.P. Weitekamp,* California Institute of Technology

NMR Spectroscopy is the premier spectroscopic method used for identification of chemical compounds. A miniaturized portable NMR spectrometer is highly desirable for field investigation of materials and in-situ planetary exploration. We are developing a novel microfabricated force-detected nuclear magnetic resonance (FDNMR) spectrometer with predicted sensitivity superior to conventional NMR at micron scales. This higher sensitivity arises from the signal-to-noise ratio scaling as d@super 0.5@ for the force detection technique, and as d@super 2@ for conventional NMR (d: sample diameter). Other force detection approaches suffer from broadening of the NMR lines and losses in sensitivity due to the magnetic field gradient imposed on the sample. We overcome this problem by producing a homogenous magnetic field across the sample using a symmetric magnet assembly. Our FDNMR detector consists of a harmonic oscillator comprised of a detector magnet mounted on a microfabricated Si beam. The detector magnet sits within an annular magnet and thus provides a uniform magnetic field over the entire sample volume. Rf pulses applied to the sample modulate the dipole-dipole interaction between the nuclear magnetic moment of the sample and the detector magnet at the mechanical resonance frequency of the oscillator. We detect the resulting motion of the mechanical oscillator at the Brownian-motion limit using a fiber-optic interferometer. In this paper, we present the microfabricated detector assembly of the MEMS-based force-detected nuclear magnetic resonance (FDNMR) spectrometer.

10:20am **MN-TuM7 Frequency-Tuning for Control of Parametrically-Resonant Mass Sensors*, W. Zhang*,** *K. Turner,* University of California, Santa Barbara

Parametric-resonance based mass sensing leads to increased sensitivity over other resonant methods@footnote 1@. In this work, we present a frequency-tuning approach to measuring mass change in an ultra-sensitive mass sensor. This scheme drives the oscillator using an electrical signal with fixed frequency and tunes the natural frequency to match the driving frequency by feeding back a DC offset to the sensor. Instead of monitoring frequency shift of oscillation in a micro-oscillator, mass change in the sensor can be detected by measuring the DC offset shift, making the sensor amenable to closed-loop control. Different from conventional harmonic resonance based mass sensor, this mass sensor detects mass change in a micro-oscillator based on parametric resonance phenomenon@footnote 1@. In a prototype mass sensor with natural frequency of 83k Hz, less than 1 Hz of frequency shift has been measured at air pressure, which is equivalent to 0.0012% of the mass of the micro-oscillator (less than 1 pg mass change in this prototype mass sensor). Due to the configuration of the micro-oscillator, which is driven by a pair of non-interdigitated electrodes, the natural frequency can be tuned by changing the DC offset in driving electrical AC signal. Since the frequency of parametric resonance at the stability boundary is related to natural frequency (doubled), the parametric resonance frequency can be tuned by DC offset feedback as well. By matching the fixed frequency of driving electrical signal with parametric resonance frequency using DC offset, the actual natural frequency change, and the mass change, can be found from monitoring shifts in the DC offset. This scheme and the prototype mass sensor has been built and tested. Potential applications include water quality monitoring, gas leakage sensing, and bio sensing, such as DNA, protein, and virus assay. @FootnoteText@ @footnote 1@W. Zhang et al, Sens. Actuators A, Phys., 102/1-2 (2002).

10:40am **MN-TuM8 Field Emission from a Tungsten MEMS Structure*, D. Cruz,*** UCLA/Sandia National Laboratories*; J.P. Chang,* University of California, Los Angeles*; M.G. Blain,* Sandia National Laboratories

We have investigated the field emission properties of free-hanging tungsten MEMS structures. The structures act as electrodes for a Paul ion trap. The ion trap consists of two end cap electrodes, a ring electrode, and a detector, fabricated in seven layers of tungsten molded about SiO2 and then released to realize a free-hung structure. In this work, different ion trap sizes (inner ring electrode radius of 1 and 1.5um) and three different sized arrays (1e4, 1e5 and 1e6 traps) were fabricated and tested for field emission. To test whether field emission may be a problem during the operation of the ion trap, voltage was applied between the outer edge of one of the end caps and the inner edge of the ring electrode. Since electrode separations are on the order of 0.5um and electrode edges are sharp, field emission may occur if a suitably large potential difference is applied. The arrays were tested at atmospheric pressure and under vacuum, 1e-6 torr. The atmospheric tests showed turn-on voltages of 150V for the 1 and 1.5um traps. Currents of 3uA were achieved for the 1um trap 1e6 array at 300V. The vacuum tests showed turn-on voltages of 200V, and lower currents at 300V for the 1um trap array. The current-voltage responses were fitted well to the Fowler-Nordheim characteristics, confirming the field emission from the devices. The difference in current between the test conditions, however, suggests a breakdown discharge at atmosphere pressures. A stable emission was obtained at 300V for 5 min. in vacuum for the 1um trap 1e6 array. The measurements show that field emission will not be an issue for operation of the traps at the required rf amplitudes; however, the results suggest an interesting alternative application for such structures as field emission devices. *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 **MN-TuM9 Suspended Waveguide-Based Tunable Integrated Optical Filters on Indium Phosphide MEMS Platform***, **M. Datta**, M.W. Pruessner, D.P. Kelly, R. Ghodssi,* University of Maryland, College Park

We propose widely-tunable planar-waveguide-based integrated optical filters on a monolithic InP platform with on-chip parallel-plate capacitive MEMS actuation as the tuning mechanism. These compact (2 mm x 1 mm), fiber-coupled, batch-fabricated filters are perfectly suited for low-cost wavelength division multiplexing optical networks. Each device consists of a moving input waveguide, a fixed output waveguide, deep-etched (>5 micron) Distributed Bragg Reflector (DBR) input and output mirrors integrated with the waveguides, an orthogonal suspension-beam, and a pair of fixed electrodes. All the components are processed monolithically using projection photolithography and methane/hydrogen reactive ion etching, followed by a sacrificial etching step in order to render the input waveguide movable as well as to prevent optical losses due to substrate-leakage (the suspended waveguide approach). InP is etched in multiple cycles, periodically removing the polymer by-products with oxygen plasma to ensure vertical sidewalls with acceptable roughness (

11:40am **MN-TuM11 Use of Plasma Polymerisation Process for Fabrication of Micro Electromechanical System (MEMS) for Micro-Fluidic Devices***, **M. Dhayal**, H.G. Hyung,* Dongshin University, South Korea*; H.J. Lee,* Chonnam National University, South Korea*; J.S. Choi,* Dongshin University, South Korea

In recent years the need for nano electromechanical system (NEMS) and micro electromechanical system (MEMS) devises in chemistry, biology and medical field has increased the interest of researcher to improve and develop new fabrication techniques to capable of building 3D structures with materials othe than silicon or with silicon. In our research we are developing a well-controlled plasma polymerisation process reator to fabricate NEMS and MEMS devises. A comparison of performance of MEMS fabricated using conventional techniques such as photolithography and reactive ion etching in our study has been also investigated. These devises are planed to use for fabrication of micro pumps for micro-fluidic devices.

Nanometer-scale Science and Technology
Room 213D - Session NS-TuM

Nanotube Processing and Composite Materials

Moderator: S. Evoy, The University of Pennsylvania

8:20am **NS-TuM1 Controlled Fabrication and Modification of Organized Carbon Nanotube Architectures***, **Y.J. Jung**,* Rensselaer Polytechnic Institute, U.S.A*; R. Vajtai, N. Chakrapani, G. Meng, P.M. Ajayan,* Rensselaer Polytechnic Institute*; Y. Homma, Y. Kobayashi,* NTT Basic Research Laboratories*; T. Ogino,* Yokohama National University, Japan

An overview of our results on the controlled fabrication and modification of organized carbon nanotube architectures will be presented. The talk includes strategies for building suspended single-walled carbon nanotubes (SWNTs) forming self-directed networks on nano-scale patterned substrate using chemical vapor deposition (CVD). We elaborate the straightening process of nanotubes in the networks suspended on Si pillars by Ga ion irradiation in a Focused Ion Beam (FIB). Beyond the morphological changes of the nanotubes and nanotube bundles we will present our conclusions for carbon atom ejection and compare with previous electron beam and ion beam irradiation experiments. Although ion irradiation induces defective structures into the nanotube lattice, as micro-Raman mapping shows, the form and dimensions of the nanotubes remain close to that of the original grown morphology. To demonstrate another nanostructure modification we will discuss the formation of intriguing two-dimensional cellular foams from capillarity-induced perturbations during the drying of vertically aligned multi-walled carbon nanotubes (MWNT) architectures with the mechanisms giving rise to pattern formation and methods of controlling the structure and orientation. Similarly, we will briefly present our latest results for organized assembly of multiwalled nanotubes into various 2-D and 3-D structures on planar substrates as well as within anodic porous aluminum oxide templates.

8:40am **NS-TuM2 Growth of Arrays of mm Long, Straight Single-Walled Carbon Nanotubes***, **Z. Yu**, S. Li, P. Burke,* UC Irvine

In this work, we demonstrate the growth of arrays of 1.5 mm long, straight single walled nanotubes fabricated using a single furnace with methane and H2 as the feedstock. Recently Huang et al[1] have fabricated 3.7 mm long single walled carbon nanotubes using a two-furnace, dual temperature growth system with CO and H2 as the feedstock. Our work shows arrays of long, straight nanotubes can be grown in a single furnace system. Using a home-built CVD system based on a 3 inch Lindberg furnace, we have synthesized long, straight nanotubes using CVD. The catalysts were prepared as follows: First, a lithographically patterned Ti(50 nm)/Au(200 nm) metallization layer is deposited and patterned using e-beam evaporation onto a Si wafer. Next, an aqueous solution containing nanoparticle catalyst is deposited and lifted off onto only the patterned Au. The growth procedure was as follows: First, the sample was heated to 900 C in Ar. Next, H2 was flowed for 10 minutes. Next, methane/H2 mixture was flowed for 15 minutes to activate the growth.Post-growth characterization was carried out with SEM. AFM growth from nanotubes grown under similar conditions in our lab yielded diameters of 1.5 nm. The growth results indicate an aligned array of nanotubes (6) with pitch of 50 microns and length of at least 200 microns. 3 of the 6 nanotubes were 1.5 mm in length. The growth of the longer nanotubes was terminated only by the presence of a neighboring catalyst site. With properly designed catalyst geometries with room to grow, cm long single walled nanotube growth should be possible. In the future it should be possible to grow 2d arrays by rotating the wafer and carrying out a second growth run. By engineering the nanotube pitch, ultra-dense electrical circuitry could be fabricated. @FootnoteText@ [1] S. Huang, B. Maynor, X. Cai, J. Liu, â?oUltralong Well-Aligned Single-Walled Carbon Nanotube Architectures on Surfacesâ?�, Advanced Materials, vol. 15, pp. 1651-1655, 2003.

9:00am **NS-TuM3 Low-temperature Synthesis of Aligned Carbon Nanotubes by Hot-Filament Assisted DC Plasma CVD***, **Y. Watanabe**, Y. Hayashi, S. Nishino,* Kyoto Institute of Technology, Japan

Carbon nanotubes (CNTs) are expected to be used for the field emitters of field emission display (FED) because their high aspect ratio and small radius of curvature lead to large electric-field enhancement at their tips resulting in low operating voltage for electron emission. The synthesis method of vertically aligned CNTs in low temperature below the softening point of a glass substrate should be developed to apply CNTs to field emitters of FED. Motivated by such a background, we carried out experiments of synthesis of CNTs in low temperature by hot-filament assisted DC plasma chemical vapor deposition (HF/DC-PCVD)@super 1@. The growth method and conditions were as follow. First a Co foil substrate was heated by hot tungsten filaments in H@sub 2@ atmosphere. Then after 10 min pretreatment in a H@sub 2@ plasma, CH@sub 4@ gas was added for the growth of nanotubes. DC voltage of -450V was applied to the substrate with the hot-filaments grounded. During the growth, substrate temperature was controlled about 500°c, the gas pressure was 20Torr, and growth time was 10 min. Well-aligned CNTs about 60 nm in diameter were observed by scanning electron microscopy in the density of about 10@super 9@ cm@super -2@ on the surface of the substrate. We have succeeded to synthesize well-aligned and high density carbon nanotubes on Co substrate at 500°c. @super 1@Y.Hayashi, T.Negishi, and S.Nishino, J. Vac. Sci. Technol. A 19(2001) 1796.

9:20am **NS-TuM4 Theoretical Study of Catalytic Growth Single-Walled Carbon Nanotubes***, F. Ding, K. Bolton, **A. Rosen**,* Goteborg University and Chalmers, Sweden

Molecular dynamics (MD) simulations based on an empirical potential energy surface (PES) were used to study iron catalyzed nucleation and growth of single-walled carbon nanotubes (SWNTs). The simulations show that SWNTs grow from the iron-carbide particle at temperatures between 800 and 1400 K, whereas graphene sheets encapsulate the particle at temperatures below 600 K and a three-dimensional (3D) soot-like structure is formed above 1600 K. The simulations also reveal other details of the growth mechanism. For example, it is seen that the growing SWNT maintains an open end on the FeC particle due to the strong bonding between the SWNT end atoms and the particle. The SWNT-particle enthalpy is minimized when the SWNT and FeC cluster have similar diameters. This leads to the growth of SWNTs that have similar diameters to the metal clusters, as has been seen experimentally.

9:40am **NS-TuM5 Controlling and Modeling the Interphase in Polymeric Nanocomposites**, ***L.C. Brinson****, H. Liu, T. Ramanathan,* Northwestern University **INVITED**

Polymeric nanocomposites made by incorporating small amount of nanoscale inclusions into polymer matrices exhibit dramatic changes in thermomechanical properties over the pure polymers. Because the properties of the nanoscale fillers can be extraordinary, even small volume fractions can result in significant changes.. Enhancing the effect is the extremely significant role that the interphase plays in these systems. Given the enormous surface to volume ratio for nanoparticles, the interphase volume fraction can dwarf that of the inclusions themselves. In this paper, experimental evidences of the existence of this interphase region are presented. We show that by properly-controlled functionalization of the nanoscale inclusions, we can impact the properties of the interphase region and consequently control the properties of the nanocomposites. In conjunction with the experimental results, the viscoelastic behavior of multi-phase polymeric nanocomposites is modeled using a novel hybrid numerical-analytical modeling method that can effectively take into account the existence of the interphase region. This hierarchical modeling approach couples the finite element technique and micromechanical approach and operates at low computational cost. Comparison between experimental and modeling results is reported.

10:20am **NS-TuM7 Wetting of Individual Carbon Nanotubes with Organic Liquids**, ***A.H. Barber****, S.R. Cohen, H.D. Wagner,* Weizmann Institute of Science, Israel

Carbon nanotubes show promise as reinforcements in polymer composites. For effective reinforcement, good adhesion between the nanotube and polymer is necessary. Adhesion at a polymer-nanotube interface involves many different types of bonding mechanisms, with wetting of fibers by the liquid polymer regarded as a necessary, but not a sufficient prerequisite for adhesion. Here we present a new experimental method to investigate the wetting behavior of single carbon nanotubes under ambient conditions. Carbon nanotubes, bound to probe tips in a scanning probe microscope are controllably dipped into various organic probe liquids. The changes in force due to the wetting of single carbon nanotubes thus can be accurately measured, giving insights on the interaction between liquid and nanotube. In particular, liquid-carbon nanotube contact angles are measured, which can be interpreted with respect to the nanotube surface characteristics. Using an Owens and Wendt analysis, the polar and dispersive components of the interaction can be separated. Our results show that the surface of the carbon nanotube displays hydrophilic behavior, in contrast to hydrophobic graphite surfaces. This project was supported by the (CNT) Thematic European network on 'Carbon Nanotubes for Future Industrial Composites' (EU), the Minerva Foundation, the G. M. J. Schmidt Minerva Centre of Supramolecular Architectures, and by the Israeli Academy of Science. H.D. Wagner is the recipient of the Livio Norzi Professorial Chair.

10:40am **NS-TuM8 Impregnation of Osmium Dioxide to MWCNTs and Improvement of the Electron Emission Characteristics**, ***T. Noguchi****, M. Shimamoto, M. Nishiwaki,* KEK, Japan; *K. Tatenuma,* KAKEN Inc., Japan; *S. Kato,* KEK, Japan

Osmium dioxide impregnation to MWCNTs was attempted in order to improve the electron emission characteristics. OsO@sub 2@ similar to RuO@sub 2@ has desirable properties including high conductivity (6x10@super -5@ @ohm@cm at 300K), high catalytic performance, and good chemical and physical stabilities. In this study, OsO@sub 2@ impregnation to MWCNTs was conducted by utilizing osmium tetraoxide in a solvent at ambient temperatures and pressures. When compared to MWNTs without impregnation treatment, those MWCNTs impregnated with OsO@sub 2@ have superior and more efficient electrical characteristics with stable emission at a lower electric field as observed for RuO2 impregnated MWCNTs.

11:00am **NS-TuM9 Electron Emission Property from MWCNTs with Subnano Ruthenium Dioxide Clusters and with High Adhesivity on Substrate - High Current Endurance Test in UHV and Influence of H@sub 2@O or CO -**, *M. Shimamoto, T. Noguchi, M. Nishiwaki,* KEK, Japan; *K. Tatenuma,* KAKEN Inc., Japan; ***S. Kato,*** KEK, Japan

Applications of MWCNTs to FEDs, electron sources of electron accelerators and surface analytical tools, and vacuum tubes for microwave amplifier, X-ray, light tube and so on require a high current density of its electron beams, a low threshold of electric field staring the field emission and a long life time with the emission. We reported the achievement of a remarkalbly high DC current density close to 300mA/cm@super 2@ with a threshold electric field of 2V/µm using new technologies of subnano RuO@sub 2@ clusters on MWCNTs surface and of high CNT adhesivity on metalic substrate. An outstanding electron emission property achieved after those treatments would be explainable based on both further increase emission points due to the subnano clusters not only from MWCNT ends but also from strongly bent wall and better thermal conductivity resulted from the heat treatment. Reduction of work function of CNT owing impregnation of RuO@sub 2@ might contribute higher field emission current density as well. Base pressure of XHV should be also big help to make sure reasonable MWCNT life at very high emission current to drastically reduce physical and chemical ion sputtering. In this paper, endurance running tests of MWCNTs in UHV up to 700 hours with a relatively high DC current of 50 mA/cm@super 2@ and degradation of the field emission characteristics due to residual gas such as H@sub 2@O or CO are focused.

11:20am **NS-TuM10 Synthesis of Y-Junction Singlewall Carbon Nanotubes**, ***Y.C. Choi****, W. Choi,* Florida International University

Y-junction singlewall carbon nanotubes were synthesized on thermally oxidized silicon substrates by chemical vapor deposition. Molybdenum, titanium, or zirconium-doped iron nanoparticles supported by aluminum oxide were used as catalysts for the synthesis. Most of singlewall carbon nanotubes have branches, forming Y-junctions. Transmission electron microscopy confirmed the formation of singlewalled structures of Y-junctions with diameters ranging from 2 nm to 4 nm. The density of Y-junctions could be controlled simply by variation of spinning rate when spin coating of catalyst soultion was carried out. It was found from radial breathing mode peaks in Raman spectra that our sample has both metallic and semiconducting nanotubes, indicating the possible formation of Y-junctions with different electrical properties. The growth mechanism based on experimental results will be further proposed.

11:40am **NS-TuM11 Surface-Programmed Assembly Process of Large-Size Multi-Wall Carbon Nanotubes and Its Mechanism**, ***J. Im****, M. Lee, S. Hong,* Seoul National University, South Korea

Recently, the surface-programmed assembly (SPA) process that utilizes surface molecular patterns to guide the assembly of single wall carbon nanotubes (SWCNT) has been reported (Nature 425, 36 (2003)). Herein, we show that the SPA method can be utilized to assemble even large-size multi-walled carbon nanotube (MWNT) which is as large as 30nm in diameter. In addition, we studied the mechanism of the SPA process for both SWNTs and MWNTs by measuring 1) the adsorption probability distribution as a function of CNT size (diameter, length, etc.) and 2) interaction energy between molecular patterns and CNTs. This result implies that SPA method can be applied for electronic applications based on relatively large-size nanowires.

Plasma Science and Technology
Room 213A - Session PS1-TuM

Dielectric Etching

Moderator: E.A. Hudson, Lam Research Corp.

8:20am **PS1-TuM1 Polymer Formation in Fluorocarbon Etch Plasmas**, ***B. Ji****, S. Dheandhanoo, S.A. Motika, P.R. Badowski, J.R. Stets, E.J. Karwacki,* Air Products and Chemicals, Inc.

Recent investigations have shown fluorocarbon (FC) polymers play several key roles in dielectric etch plasmas. A steady state FC film is a key ingredient for etching silicon under ion bombardment. For anisotropic dielectric etching, FC films protect the photoresist mask and passivate the feature sidewalls. In recent years, the semiconductor industry have adopted heavier molecular weight and lower fluorine to carbon ratio gases, such as c-C@sub 4@F@sub 8@, C@sub 5@F@sub 8@, and C@sub 4@F@sub 6@ for anisotropic dielectric etching. In this study, we investigate the correlation between fluorocarbon molecular structure and

FC film property. We employ mass spectrometry to determine electron impact fragmentation patterns of various fluorocarbon molecules. We use Fourier transform infrared spectroscopy and x-ray photoelectron spectroscopy to characterize the FC polymer structure. We investigate a series of novel dielectric etch gases such as c-C@sub 4@F@sub 8@, C@sub 4@F@sub 8@O, C@sub 3@F@sub 6@, C@sub 3@F@sub 6@O, C@sub 5@F@sub 8@, C@sub 4@F@sub 6@, and C@sub 6@F@sub 6@ etc. The results demonstrate that FC film properties depend not only on the atomic fluorine to carbon ratios, but also on the bonding structures in the molecules. Finally, we correlate the molecular fragmentation patterns and FC film properties to anisotropic dielectric etch performances of various gases.

8:40am **PS1-TuM2 Reduction of Line Edge Roughness for 90nm Technology Node for Contact and Trench Etched Features**, ***D. Farber***, Texas Instruments, Dallas; *W. Dostalik, B. Goodlin, R. Kraft, T. Lii,* Texas Instruments

For the 90nm technology node, methods for reducing line edge roughness (LER) during dielectric etch are shown. Two particular, distinct cases are demonstrated here: 1) contact holes etched in phosphorus-doped glass (PSG), and 2) trench lines in organo-silicate glass (OSG) low-K dielectric for damascene Cu interconnect. For both cases, an etch strategy is developed to deal with the inherent roughness and granularity of 193nm photoresist while maintaining adequate CD control and resist thickness margin. Using an image processing technique, an effort is made to quantify the degree of LER associated with the processes.

9:00am **PS1-TuM3 Effect of Non-sinusoidal Bias Voltage Waveforms on Ion Energy Distributions and SiO@sub 2@/Si Etch Selectivity in Fluorocarbon Plasmas@footnote 1@**, ***A. Agarwal***, *M.J. Kushner,* University of Illinois at Urbana-Champaign

During plasma etching, ion energy distributions are typically coarsely controlled by varying the amplitude of a rf sinusoidal bias voltage and/or controlling the dc bias. The resulting ion energy distribution (IED) is often broad compared to the differences between threshold energies of surface processes. Controlling the width of the IED can potentially help maintain critical dimensions of features and improve selectivity. In high-plasma density, low gas pressure systems, sheaths are typically collisionless and so additional control over IEDs can be obtained by controlling the sheath voltage. In this regard, non-sinusoidal bias waveforms have been proposed as a means to tailor the IEDs.@footnote 2@,@footnote 3@ In this talk, we report on results from a computational investigation of IED control by using a tailored non-sinusoidal bias voltage waveform. A 2-dimensional plasma equipment model has been linked with a Monte Carlo feature profile model to assess the consequences of the resulting IEDs on the selectivity of etching SiO@sub 2@ to Si in fluorocarbon ICP plasmas and capacitively coupled plasmas. The most stringent control over the IEDs is obtained at lower frequencies where sheath crossing times are short compared to the rf period and in gas mixtures where the masses of the ions are similar. Slightly more collisional plasmas (provided the sheath remains collisionless) also provide more stringent control by reducing the energy of ions entering the sheath proper. @FootnoteText@ @footnote 1@ Work supported by SRC and NSF. @footnote 2@ S. B. Wang and A. E. Wendt, J. Vac. Sci. Technol. A, 19, 2425 (2001) @footnote 3@ S. Rauf, J. Appl. Phys., 87, 7647 (2000).

9:20am **PS1-TuM4 Dielectric Processes Enhancements Using Multifrequency Sheath Modulation**, ***S.C. Shannon***, *A.M. Paterson, T. Panagopoulos, D. Hoffman, J.P. Holland,* Applied Materials, Inc.; *D. Grimard,* University of Michigan

Dual frequency capacitive discharges have become the new standard in dielectric etch processing. Typically, frequencies are selected such that bulk plasma dissociation and plasma sheath dynamics can be independently controlled. Recently, dual frequency development has focused on the interaction of the two frequencies in the sheath surrounding the plasma. In this paper, a model is presented where a symetric discharge is driven by an RF current with multiple frequency components. The impact of these multifrequency sheath dynamics on ion energy distribution and the process tunability in dielectric etch processes using this technology is presented.

9:40am **PS1-TuM5 A Novel Etching Process Employing Pulse-Modulated Electron-Beam-Excited Plasma for Fabrication of Micro-Optical Devices**, ***K. Takeda***, Nagoya University, Japan; *Y. Tomekawa, T. Ohta,* Wakayama University, Japan; *K. Yamakawa,* Nagoya University, Japan; *M. Ito,* Wakayama University, Japan; *M. Hori,* Nagoya University, Japan

Recently, micromachining of optical devices such as core lens on the edge of optical fiber attracts much attention. In this process, the fast atomic-beam etching (FABE) or the ion-beam etching (IBE) has been employed, since the conventional reactive plasma etching cannot be employed as the radio-frequency self-biasing is not efficiently supplied to the thick dielectric materials. However, the etch rates of FABE and IBE are typically around a few tens nm/min, which are very low compared with the reactive ion etching. Therefore, novel processes to realize the higher etch rate are strongly required to reduce the processing time. We have proposed a SiO@sub2@ etching employing an electron-beam-excited plasma (EBEP) for the fabrication of micro-optical devices. The dc-EBEP have realized the high etch rate without any additional bias power supply. However, it had problems such as the thermal damage of the photo resist, non etch-uniformity and instability of plasmas. In this study, we have developed a novel etching process for the fabrication of micro-optical devices employing a pulse-modulated EBEP and have investigated the etching characteristics. Plasma was generated at a total pressure of 0.27Pa and the fed gases were C@sub4@F@sub8@/Ar, a discharge current of 25A and an electron beam acceleration-voltage (V@subA@) of 100V with a pulse-modulation frequency of 50kHz and 50% duty ratio. The pulse-modulated EBEP have been found to have a great potential to realize the high etch rate of 375nm/min with 0.75mm hole-pattern and improve some problems in the dc-EBEP. Moreover, from the results of the optical emission spectroscopy, F atom density was reduced with the decrease of the duty ratio of V@subA@. Therefore, We performed the anisotropic SiO@sub2@ etching with a high rate by the ion assisted etching without any self-biasing power supply. Consequently, the micro-fabrication of core lens on the edge of optical fiber was successfully carried out.

10:00am **PS1-TuM6 Surface Kinetics Modeling for Silicon Oxide and OSG Etching in Fluorocarbon Plasmas**, ***O. Kwon***, *B. Bai, H.H. Sawin,* Massachusetts Institute of Technology

Fluorocarbon plasma for silicon oxide or OSG etching is a complicated system involving many ion and neutral species. Depending on the plasma condition, many difficulties arise such as RIE lag, etch stop, and low selectivity to photoresist. For a better understanding of the process it is necessary to have an appropriate surface kinetics model which includes simultaneous etching and deposition. We have developed a novel surface kinetics modeling approach, Translating Mixed Layer (TML) model that is based on the assumption that the surface layer is a well-mixed region due to energetic ion bombardments. The mixed layer thickness is given the depth associated with ion bombardment, i.e. ~2.5 nm. The etching and deposition reactions are modeled based on the elemental composition of this layer using a lumped kinetic model. The lumped kinetic model was constructed and verified using measured oxide etching yield data determined by quartz crystal microbalance (QCM) in conjunction with plasma neutral and ion concentrations/fluxes determined by mass spectrometry of C2F6 and C4F8 discharges over broad ranges of process conditions. Etching chemistries with low atomic fluorine concentration (e.g. C4F8 chemistry) exhibit etching yields that are sensitive to compositional change in the plasma. In chemistries with high atomic fluorine concentration (e.g. C2F6 chemistry); however, the etching yield is less sensitive to compositional change in the plasma. Based on the measurements and the simulation, a lumped oxide etching surface kinetics model was constructed. In this model, adsorbed fluorocarbon species act as the etchant and the etching yield is determined by the composition of the surface layer. Atomic fluorine acts as a fluorocarbon etchant to control the etching yield. The model was also applied to OSG etching with fluorocarbon chemistry. The model successfully predicts the etching characteristics of OSG film.

10:20am **PS1-TuM7 Study on Self-aligned Contact Oxide Etching Using C@sub 5@F@sub 8@/O@sub 2@/Ar and C@sub 5@F@sub 8@/O@sub 2@/Ar/CH@sub 2@F@sub 2@ Plasma**, ***S.B. Kim***, *D.G. Choi, D.S. Kim, Y.W. Song,* Hynix Semiconductor Inc., Korea; *C.I. Kim,* Chung-ang University, Korea

A self-aligned contact (SAC) technology is developed for application of electrical contacts between the local interconnection and the silicon diffusion regions (or plug pad) from 0.18µm device. The commercial memory devices have capping (or spacers) nitride (Si@sub 3@N@sub 4@) for protection of Word Line (or Bit Line) and nitride thin film layer for etching stop of SAC. Recently, the problems of SAC etch process in ULSI devices of sub 0.1µm-design rule are low selectivity to nitride and etching-stop due to high aspect ratio of contact hole. The key issue of SAC etch process is control of polymer generation. In this study, the characterizations of SAC oxide etching are investigated with C@sub 5@F@sub 8@/O@sub 2@/Ar and C@sub 5@F@sub 8@/O@sub 2@/Ar/CH@sub 2@F@sub 2@ plasma. As the mixing ratio of O@sub 2@ on the C@sub 5@F@sub 8@/Ar/O@sub 2@ increase, the amount of polymer decreases and the ability of contact etching increases, the effect CH@sub 2@F@sub 2@ addition on SAC oxide (SiO@sub 2@) etching in C@sub 5@F@sub 8@/Ar/O@sub 2@ is that etch rate of oxide in the contact hole increases about 7%, and the selectivity of oxide to nitride increase, specially that to nitride of contact bottom for SAC etch stopping increases. The selectivity of oxide to nitride increases with increasing of plasma source power or with decreasing of bias power. SAC patterned wafers were characterized using top-down critical dimension scanning electron microscopy (CD-SEM), cross-section SEM, and transmission electron microscopy (TEM). To analyze the effect of various parameters on the C@sub 5@F@sub 8@/Ar plasmas, we investigated the chemical species in the gas phase with an optical emission spectroscopy (OES). The components of polymer were investigated with transition electron microscopy - energy dispersive X-ray (TEM-EDX) and auger electron spectroscopy (AES). X-ray photoelectron spectroscopy (XPS) studies have analysis of real polymer topology on contact bottom and side wall.

10:40am **PS1-TuM8 Advanced Inductive Plasma Etcher for Low-k Materials and Oxide***, **G. Vinogradov**, A. Kelly, V.M. Managarishvilil, Y. Hirano,* FOI Corporation, Japan

A new kind of ICP dielectric etcher has been tested on a variety of materials and patterns and showed produciton worthy results. There is presently only one type of commercial 300-mm equipment for advanced SiO@sub 2@ dry etch: narrow-gap capacitive. Flat inductive plasma sources do not provide radial uniformity in narrow gap designs. An increase of the discharge gap (volume) improves uniformity but substantially increases gas residence time thus decreasing selectivity to photoresist. Another problem is instability of known flat ICP etchers due to capacitive sputtering of the dielectic plate separating ICP coils from plasma volumes. Flat inductive sources, therefore, were not yet successful for advanced oxide etch. A novel inductive narrow-gap 300-mm GroovyICP@super TM@ plasma etcher having substantially flat geometry for advanced etch of low-k materials (organic and inorganic) and oxide in one multiprocess chamber was developed and tested in production. It incorporates three mutually embedded geometrically separate and independently adjustable ring-shape inductive plasma sources designed as annular grooves in a flat roof made of silicon or ceramics. Every coil/plasma ring has independent RF power supply thus achieving controllability over the radial power distribution. Process results obtained with our 300-mm etchers will be presented in order to show principal features and exclusive controllability of the new plasma source and manufacturing tools.

11:20am **PS1-TuM10 Impact of Vibrational States on Dissociation in Fluorocarbon and Hydrogenated Fluorocarbon Plasmas***, S. Adamson, K. Novoselov, A. Dement'ev, V. Kudrja,* Soft-Tec, Russia*; S. Rauf, **P.L.G. Ventzek**,* Freescale Semiconductor

Vibrational states of polyatomic molecules are known to have an important effect on the energy balance in plasmas and as such the plasma chemical kinetics. Less often considered is the impact of the population of vibrational states on individual processes associated with one species in which multiple vibrational states are often lumped. High density plasmas used for plasma processing may be characterized by relatively large gas temperatures (>700K) allowing for population of some low lying energy vibrational states. The presence of an ensemble of a few low lying energy states is significant as the cross-sections defining the transition to dissociation from states above ground may be quite different than those from ground. The dissociation processes associated with C4F6 and other CxHyFz plasmas are explored by treating the dissociation processes as bi-molecular using a diatomic model with the energies of the vibrational states being the states of the mode associated with the two pre-linked dissociating units. While not fundamental modes, they provide a means of exploring the scaling of electron impact reaction rates with temperature. Further they facilitate the exploration of assumptions built into simulations used to extract transport parameters for plasma process simulation (e.g., electron swarm simulations). In this presentation, the scaling of electron transport parameters and reaction rates for various electron impact processes with gas temperature and gas mixture are parameterized. These results are complemented with illustrative integrated equipment and feature scale simulations.

11:40am **PS1-TuM11 Measuring Macro- and Micro-loading Impact on Etch Bias***, **H.P. Stadniychuk**,* Cypress Semiconductor

Ever smaller critical dimensions (CD) and tighter budgets call for minimization of device-to-device differences in the fab. While all devices typically share the same design rule for the targeted feature on any given layer, pattern density variation became a significant contribution to the observed CD variation. In this study pattern density effect on STI (Shallow Trench Isolation) - type etch was characterized on local (hundreds of microns) and global (wafer) scales while keeping pitch the same and ARDE (Aspect Ratio Dependent Etch)-effects constant. One the challenges were to determine what constitutes the local scale and how data can be collected without using special masks. It was found that etch bias is twice more sensitive to variation in local pattern density than to the global. Methodology for proper accounting pattern density-induced CD variation in process development as well as strategies for compensating these effects will be discussed.

Plasma Science and Technology
Room 213B - Session PS2-TuM

New Gate Conductor Etching

Moderator: C. Labelle, Advanced Micro Devices

8:20am **PS2-TuM1 Study of Refractory Metal Nitrides/HfO@sub 2@ Gate Stack Etching Using Inductively Coupled Plasma***, J.H. Chen, W.S. Hwang, **W.J. Yoo**, S.H.D. Chan,* National University of Singapore, Singapore*; D.-L. Kwong,* University of Texas, Austin

Metal gates/high-K gate stacks are expected to be used for 45nm and beyond MOSFETs, replacing conventional Poly-Si/SiON gate stacks. Refractory metal nitrides (RMNs) including TaN, TiN, and HfN are being studied extensively as the promising candidates for future metal gates, because of good thermal stabilities, and suitable work functions on hafnium based high-K dielectric for CMOS devices. In this work, we investigated the etching properties of RMNs (TaN, TiN and HfN) on HfO@sub 2@ using inductive coupled plasma (ICP) of HBr/Cl@sub 2@/O@sub 2@. Results show that the etch rate of ~2800Å/min for TaN, ~2500Å/min for TiN and ~4000Å/min for HfN can be achieved at 10mTorr in HBr/Cl@sub 2@ plasma (inductive power of 400W and DC bias of 144V). Etch rates of RMNs increase rapidly with increasing ion density and energy. The dependences of etch rates of TaN, TiN and HfN on ICP parameters are different, but all are more sensitive than that of poly-Si. Etch electivity of RMNs with respect to HfO@sub 2@ was lower, comparing to poly-Si/SiO@sub 2@ gate stack structure. Adding small amount of O@sub 2@ into Cl@sub 2@ or HBr plasma enhanced the etch selectivity of RMNs with respect to HfO@sub 2@, because it can suppress the etch rate of HfO@sub 2@, without a significant change the etch rates of RMNs. Improvement of etch selectivity can be also achieved by reducing ion energy and increasing pressure. Very anisotropic profile of these three RMNs metal gates can be acquired by reducing pressure, increasing ion energy and adding more Cl@sub 2@ in the gas mixture. Optical emissions at 400-800nm wavelength were observed from RMNs etch byproducts in Cl@sub 2@ or HBr plasma, providing sharp etch end point signal. X-ray photoelectron spectroscopy analysis of etched surfaces shows that most of etch byproducts of these three RMNs etched by Cl@sub 2@ or HBr plasma are volatile at 10mTorr and 100°C, and residues are found to be mainly bromides and chlorides.

8:40am **PS2-TuM2 Line Width Roughness Reduction for Advanced Metal Gate Etch and STI Etch with 193nm Lithography in a Silicon Decoupled Plasma Source Etcher (DPSII)***, **T. Chowdhury**, H. Lee, A. Renaldo, K. Ikeuchi, A. Habbermas, B. Bruggermann,* Cypress Semiconductor*; Y. Du, M. Shen, S. Deshmukh, J. Choi,* Applied Materials, Inc.

193nm lithography has become necessary as the critical dimensions of semiconductor devices continue to scale down towards sub 90 nm dimension. From a device point of view the effects of higher Line Edge Roughness (LER)/Line Width Roughness (LWR) are studied. Metrology aspects of LER/LWR are also included in the study. From dry etching perspective, however, 193nm resist brings new challenges due to its poorer plasma etch resistance, LER/LWR and lower thickness compared to 248nm DUV resist. This paper presents a successful development of advanced 0.1µm metal gate and STI etch application using 193nm lithography on Applied Materials' decoupled plasma etcher DPSII system. Process chemistry and process parameters for nitride mask step were thoroughly explored and investigated vs LWR. Post-etch measurement of line width roughness shows an average of 6nm LWR. It was observed LWR is a strong function of etch chemistry (CHF3/CF4 based HM open vs CH2F2 based HM Open), reaction regime (15 mT vs 30 mT) and ICP vs MERIE etc. A detailed study showing methods to reduce LWR is presented in this paper. .

9:00am **PS2-TuM3 Plasma Etching of Metal/High-K Gate Stack*, A. Le Gouil,*** STMicroelectronics, France*; T. Chevolleau, G. Cunge, L. Vallier, O. Joubert,* LTM-CNRS, France*; P. Mangiagalli, T. Lill,* Applied Materials

The rapid downscaling of metal-oxide-semiconductor transistors imposes new materials for the gate stack. Metal gate electrode receives more attention than conventional poly-Si gate electrode when high permittivity material is used as the gate dielectric. In addition to the introduction of these new materials, critical dimension control of less than 3nm must be achieved for the 45 nm technological node. In this work the metal gate etching process is developed with a poly-Si/TiN stack for the gate electrode and HfO@sub2@ (3.5 nm thick) as the gate dielectric. Anisotropic and selective etching of the gate stack requires the development of a multi-step etching process. First, the silicon part of the gate is etched using an HBr/Cl@sub2@/HeO@sub2@-based chemistry. We have then studied several chemistries (Cl@sub2@ , HBr and their mixture) to etch the TiN layer anisotropically and selectively with respect to HfO@sub2@. The selectivity and surface modification of the HfO@sub2@ layer after exposition to the plasmas have been studied by X-ray Photoelectron Spectroscopy and AFM. While highly anisotropic etching can be observed in pure Cl@sub2@ plasmas, a very rough HfO@sub2@ surface is observed in this case, partially due to the presence of TiO@subx@ residues on the HfO@sub2@ surface. In addition the selectivity toward HfO@sub2@ is poor. By contrast HBr provides a higher selectivity with less roughness. Hence using a mixture of HBr/Cl@sub2@ appears to be the best strategy to achieve both anisotropic and selective etching of TiN film over HfO@sub2@. Finally, a complete metal gate process requires HfO@sub2@ removal after the gate definition. We will show that this high temperature plasma process can seriously damage the gate profile due to the lack of passivation layer on the TiN sidewalls (undercutting is observed). This suggests that a protection layer must be formed after or during TiN etching in order to protect the metal gate before removal of the dielectric of the gate.

9:20am **PS2-TuM4 Etching Ruthenium with O2- and Cl2-Containing Inductively Coupled Plasma*, C.-C. Hsu,*** *D.B. Graves, J.W. Coburn,* University of California, Berkeley

Ruthenium (Ru) plasma etching has been studied using inductively coupled plasma (ICP) with O2- and Cl2-containing plasma, with the objective of understanding the relationship between plasma characteristics and the competition between wall deposition of etch by-products and the creation of volatile etch by-products that flow into the downstream. The ICP was characterized by in-situ ion and neutral mass spectrometers, a chamber wall-mounted quartz crystal microbalance, optical emission spectroscopy, a wall-mounted ion flux probe, and an FTIR spectrometer in the turbomolecular pump foreline. Ru films were etched from 150 mm diameter wafers placed on a rf-biased substrate. Ru can be etched readily by Ar and O2-containing plasma. Cl2 addition results in significant changes in etch rate, wall deposition behavior, and downstream etch product composition. With 10 sccm Ar and 10 sccm O2 at 10mT pressure and 100V bias voltage, a 60 angstroms/min etching rate was observed. In addition, without Cl2 addition, no RuO4 was observed in the foreline, and almost all etch by-products were deposited on the chamber wall. With Cl2 addition (Ar/O2/Cl2 plasma), the etching rate increased by a factor of 5, RuO4 was observed downstream by FTIR, and virtually zero wall deposition rate was observed. One interpretation of the observations is that chlorine addition to the Ar/O2 plasma results in a more volatile Ru-oxychloride etch product, increasing both film etch rate and chamber wall re-etch rate.

9:40am **PS2-TuM5 Ru Etching Characteristics in Capacitively Coupled Ar/Cl@sub 2@/O@sub 2@ Plasma*, S. Rauf,*** *P.L.G. Ventzek, V. Vartanian, B. Goolsby,* Freescale Semiconductor*; S. Burnett,* International Sematech*; L. Chen,* Tokyo Electron America Inc.

As the semiconductor industry attempts to replace the traditional gate dielectric, SiO@sub 2@, with higher-@kappa@ dielectrics (e.g., HfO@sub 2@), a thin metal layer need to be introduced in-between poly-silicon and gate dielectric to control conductor-dielectric interface properties. Ru is one metal that is being considered for this application. Along with electrical characteristics, the metal etching properties and compatibility of metal etch chemistry with other materials will determine how suitable a particular metal is for use in transistor gates. This paper describes a combined experimental and computational modeling investigation of Ru etching characteristics in a commercial dual frequency capacitively coupled Ar/Cl@sub 2@/O@sub 2@ plasma. Experiments explored the impact of gas mixture, RF power, gas pressure, and wafer temperature on Ru etch rate. Fourier transform infrared spectroscopy was also used to analyze effluents downstream from the plasma. Computational modeling was done using Io, a 2-dimensional plasma equipment simulation code. Plasma modeling results and blanket wafer etch rates were used to put together the Ru etch mechanism. Results indicate that reactive ion etching is the dominant Ru etch process, where O is first absorbed on Ru surface (generating RuO@sub x@) and the resulting compound is sputtered by energetic ions. The model captures experimental etch rate trends well at low gas pressures, but there is disparity between model and experiment at higher pressures. This difference is likely due to thermalization of sputtered Ru and RuO@sub x@ in the plasma, whose plasma chemistry is not well understood and, therefore, not accurately captured in our plasma chemical mechanism.

10:00am **PS2-TuM6 An Isotropic SiGe Etch Process for Fabrication of Silicon-on-Nothing Transistors*, T. Sparks,*** *S. Rauf,* Freescale Semiconductor, France*; G. Cunge, L. Vallier,* LTM-CNRS, France

As the device dimensions are shrinking, the development of new transistor structures is essential to meet the ITRS roadmap device performance specifications. One such device, the Si-on-nothing (SON) transistor, utilizes a sacrificial SiGe epitaxial layer underneath a thin transistor active channel region. The SiGe layer is removed using a lateral isotropic etch process. Isotropic chemical downstream etch processes for SiGe removal suffer from high etch rates, low selectivity to Si and lack of insitu monitoring processes such as optical emission analysis. An alternative approach for lateral SiGe etching has been developed utilizing an inductively coupled plasma (ICP) operating in the 'remote' plasma mode, and it is described in this presentation. The etch process was designed using a combination of computational modeling and experiments. The Hybrid Plasma Equipment Model (HPEM) from the University of Illinois was utilized for plasma modeling and process design, and experiments in a commercial ICP reactor were used to confirm the predicted conditions. The plasma model was also coupled to a string-based feature scale model, where the etch mechanism was based on blanket wafer etching experiments and information available in literature. Etching was conducted in CF@sub 4@ containing plasmas, which will generate SiGe etchants (e.g., F) as well as polymer precursors for Si (e.g., CF@sub 2@). Possible mechanisms were investigated to understand the observed high isotropic etch selectivity of SiGe to Si. Process modeling also identified an intermediate gas pressure regime where plasma was localized close to the inductive coils away from the substrate. If the plasma is operated in this gas pressure regime without RF bias, ion energy flux at the substrate was small while flux of neutral etchants and polymer deposition precursors was reasonable. The resulting SiGe process therefore offered good selectivity to Si and a controllable etch rate.

10:20am **PS2-TuM7 X-ray Photoelectron Spectroscopy Study on Walls Coatings and Passivation Layers Generated on Sidewalls Trenches during Shallow Trench Isolation Processes.*, C. Maurice,*** *B. Pelissier, G. Cunge, O. Joubert,* LTM-CNRS, France

For IC technology where delineating ever-finer structures is critical, wafer-to-wafer reproducibility is essential. Inherent to plasma processes, the coatings deposited on the reactor walls can disturb reproducibility by influencing the plasma chemistry. Simultaneously to walls coatings formation, passivation layers issued from etch products are deposited on the sidewalls of the etched patterns. These passivation layers, mandatory in obtaining controlled profiles are dependent on reactor walls conditions. This study proposes an XPS analysis of both walls coatings and of the passivation layers deposited during Shallow Trench Isolation (STI) processes. First, using a simple piece of Al@sub2@O@sub3@ floating on top of a 200 mm diameter wafer, walls conditions have been simulated and the chemical composition of the walls coatings analyzed quasi in-situ after each etching steps of the process. Secondly, using the combined effects of geometrical shadowing (allowing the screening of photoelectrons coming from the bottoms of the patterns) and of electrostatic charging, the chemical composition of the passivation layers formed on feature sidewalls has been determined. Results validate the technique even in the case of STI etching where the passivation layers are very thick. Comparison between the results obtained on the final walls coatings and passivation layers reveals in both cases the formation of SiOCl layers and thus the important correlation between the two deposits. Comparison between SiO@sub2@ and Si@sub3@N@sub4@ hard masks is performed. The impact of

CF@sub4@ addition in typical Cl@sub2@/O@sub2@ chemistries is also investigated.

10:40am **PS2-TuM8 The Control of Electrode Impedance, Gas-Injection and Wafer-Temperature Radial Profile and their Effects on Poly-Gate Etching Performance***, **M.H. Hagihara**, L.C. Chen, F.H. Higuchi, Y.T. Tsukamoto, K.I. Inazawa,* TEL*; T.T. Tatsumi, A.K. Kawashima,* Sony

The etch rate and CD radial uniformity can be effectively optimized by controlling the radial profile of the inlet gas, the plasma parameters and the wafer temperature. A 2-zone ESC is used to control the wafer temperature radial profile. The ion energy and electron density (n@sub e@) radial distribution are controlled by the wafer-electrode's VHF impedance. The variable impedance is achieved by a series LC circuit where a variable capacitor is used. SCCM POLY source-plasma is generated by 60MHz VHF power while the 13.56MHz wafer-bias accelerates the ions. The passage of the 60MHz electron towards the wafer-electrode and hence, the n@sub e@ radial profile, is strongly effected by the wafer-electrode's 60MHz impedance. In addition to the wafer-electrode's 13.56MHz bias power, the ion energy is also effected by its 60MHz impedance. The etcher is also equipped with a 2-zone gas showerhead providing radial distribution control of the neutral species. Etch data were taken for 4 poly-gate steps: fluorocarbon-based BARC etching, fluorocarbon TEOS hard mask open, fluorocarbon-based high-dope poly etching and HBr-based poly etching. A radial SW (Surface Wave) probe is used to measure the radial n@sub e@ directly above the wafer at various 60MHz impedance settings. Etch rate, XSEM profile and top-down CD uniformity are also recorded for various VHF impedance settings, 2-zone gas injection ratios and various 2-zone ESC temperature settings. Provision of these additional control knobs significantly improve the uniformity of the etch results.

11:00am **PS2-TuM9 Process Diagnostics and Optimization in Plasma Etch Chambers Using In-Situ Temperature Metrology***, **P. MacDonald**,* OnWafer Technologies, Inc.*; B. Hatcher, J.P. Holland,* Applied Materials, Inc.*; M. Welch, M. Kruger,* OnWafer Technologies, Inc.

Performance metrics in plasma etching are strongly affected by various interacting mechanisms including direct chemical reaction, reactive etching, deposition, and mask erosion. Some of these basic etch mechanisms are extremely sensitive to temperature. As a result, across-wafer temperature variations are a first order indicator of etching performance in advanced plasma etch reactors. This temperature variation is a combination of effects ranging from reactor design to individual recipe parameters. With wafer-level thermal data available, any of these factors can be modified to improve process performance. This paper establishes concrete methodologies for in-situ process optimization using a wireless sensor system. The sensor system provides the precision necessary to break the ITRS "brick-wall" of "measurement precision of wafer surface temperature,"@super1@ by combining in-situ plasma SensorWafers and an advanced diagnostic data processing suite. This paper offers multiple examples on advanced polysilicon processes that illustrate rapid, effective process optimization and ESC diagnostics. In the process optimization section, state-of-the-art polysilicon etch chambers are evaluated for critical process characteristics. The effectiveness of temporal/spatial temperature signatures as indicators of process performance is demonstrated. Wafer-level thermal data is correlated to actual device results to verify performance of the optimized process. In the ESC characterization segment, multiple leading-edge ESC designs are evaluated to ensure process transferability and performance. The effectiveness of temporal/spatial temperature signatures to quickly and easily evaluate ESC design iterations is demonstrated. These diagnostics save considerable time and effort over the current methods established for ESC fingerprinting. @FootnoteText@ @footnote 1@ ITRS: 2003, Table 6, Key Sensor Technology Requirements.

11:20am **PS2-TuM10 New Mthod to Analyse Chamber Walls Coating during Plasma Etch Processes***, **O. Joubert**, G. Cunge, B. Pelissier, C. Maurice, L. Vallier,* LTM-CNRS, France

In today's etching processes for microelectronic application the shape of the etched feature must be controlled within 5 nm. This nanometer-scale linewidth control requires a perfect process repeatability. In high density plasmas operating at low pressure it is difficult to achieve due to the deposition of organic (or mineral) layers on the reactors walls during the process. This formation of this layer on the reactor walls modifies the surface loss probability and the concentrations of radicals involved in the etching process, leading to process instabilities. However, the chemical nature of these layers, their deposition mechanism and their influence on the plasma chemistry remains poorly understood. Recently, we have developed a new and very simple method based on the fact that a small piece of Al@sub 2@O@sub 3@ floating on top of a 200 mm diameter wafer during an etch process experiences the same exposition to the plasma than the chamber walls. We have then use quasi in situ XPS measurements to have access to the chemical nature of the layers formed on the floating Al@sub 2@O@sub 3@, i.e the chamber walls, during plasma etching processes. Using this technique, we can determine accurately the chemical nature of the layers coated on the reactor walls after various etching processes including silicon and metal (TiN) gate etching. We will demonstrate that the final nature of the chamber wall coatings is strongly influenced by the presence of resist on the wafer, nature of the layers composing the gate stack and chemistries used during the different steps of the process. We will then discuss the cleaning strategies that are commonly used after gate etching processes and their limitations.

Advanced Surface Engineering
Room 303D - Session SE-TuM

Hard and Low Friction Coatings with Advanced Designs

Moderator: D. Gall, Rensselaer Polytechnic Institute

8:20am **SE-TuM1 Tribological Coatings: Synthesis, Structure, and Properties***, **D.V. Shtansky**,* Moscow State Institute of Steel and Alloys, Russia **INVITED**

Various approaches to design and evolution of tribological coatings are review and refer to our recent results on the deposition, characterization, testing, and application of multicomponent nanostructured thin films. The targets for PVD based on the systems TiN+TiB@sub 2@, Ti@sub 5@Si@sub 3@+Ti, Ti@sub 5@Si@sub 3@+TiN, TiB@sub 2@+Si, TiB@sub 2@+SiC, TiB+Ti@sub 9@Cr@sub 4@B+Cr@sub 2@Ti, CrB@sub 2@, TiB@sub 2@+TiAl+Ti@sub 2@AlN, TiC+Ti@sub 3@SiC@sub 2@+TiSi@sub 2@, TiC@sub 0.5@+ZrO@sub 2@, TiC@sub 0.5@+CaO, Ti@sub 5@Si@sub 3@+ZrO@sub 2@, and TiC@sub 0.5@+Nb@sub 2@C were manufactured by means of self-propagating high-temperature synthesis (SHS). Multicomponent films were deposited by DC magnetron sputtering of composite targets either in an atmosphere of argon or reactively in a gaseous mixture of argon and nitrogen. The BN and WSe@sub x@ films were deposited using a sintered hexagonal BN and a cold compacting WSe@sub 2@ target, respectively. The WSe@sub x@ films were deposited by pulsed laser deposition (PLD) and ion-assisted PLD technique. The microstructure and chemical composition of films were studied by means of AES, EDXS, XRD, SEM, TEM, high-resolution TEM, XPS, and EELS. The films were characterized in terms of their hardness, elastic modulus, elastic recovery, adhesion, surface topography, friction, and wear. The biocompatibility of the medical films was evaluated by both in vitro and in vivo experiments. Three groups of films are considered: 1) nanostructured hard, tribological coatings Ti-B-N, Ti-Cr-B-N, Ti-Si-N, Ti-Al-B-N, Ti-Si-C-N, Ti-Si-B-N, BN, and Cr-B-N; 2) double-layer self-lubricating/hard coatings WSe@sub x@/TiC, WSe@sub x@/TiCN, WSe@sub x@/TiSiN, and 3) biocompatible hard coatings for medicine Ti-Ca-C-O-(N), Ti-Zr-C-O-(N), Ti-Zr-Si-O-(N), and Ti-Nb-C-(N). Particular attention is paid to the analysis of the structure of the films in the nanometric scale and the evaluation of the properties of the individual nanostructures.

9:00am **SE-TuM3 New Concepts for Low-friction Coatings***, **C. Mitterer**,* University of Leoben, Austria

Hard coatings deposited by plasma-assisted vapor deposition are widely used to reduce tool wear. The presently applied transition metal nitride coatings show high friction against steels, which restricts their applicability with reduced or without coolant. Tool temperatures for different machining operations are extremely different ranging from relatively low temperatures for deep drawing to above 1000°C for dry cutting. Presently applied low-friction coatings are essentially based on diamond-like carbon and MoS@sub2@, which often begin to fail with increasing temperature, in humid atmosphere or due to oxidation. The aim of the present contribution is thus to present now concepts for low-friction coatings for different temperature ranges. Examples for low-temperature lubrication approaches to be described include Cl-alloyed TiN coatings, where low-friction coefficients are provided by the Cl-induced formation of rutile layers on top of the coating in humid air, and CrC/a-C:H, where graphitization of the a-C:H phase is responsible for low friction coefficients. Approaches for lubricant phases at high temperatures (i.e. above 600°C) are based on the formation of Magneli phase oxides, in particular

V@sub2@O@sub5@, due to oxidation of VN in Ti@sub1-x@Al@subx@N/VN superlattices or V in V-alloyed Ti@sub1-x-y@Al@subx@V@suby@N coatings. Using these concepts, friction coefficients of 0.2-0.4 against steel can be obtained for temperatures of 700°C, where lubrication is achieved by melting of the V@sub2@O@sub5@ phase. Another high-temperature low-friction approach is the application of thin top layers based on intermetallic phases on hard coatings. In particular, the Al@sub2@Au phase is stable up to 850°C without oxidation, shows a pink color and yields friction coefficients of 0.45 at 700°C. These nanoscale design approaches allow the utilization of functional properties facilitating the development of next generations hard coatings.

9:20am **SE-TuM4 Why do DLC and MoS@sub x@-based Amorphous Coatings Have Similar Friction and Wear Behavior?***, **I.L. Singer**,* Naval Research Laboratory **INVITED**

Amorphous coatings based on MoSx and hydrogenated carbon (a-C:H) exhibit dry sliding friction and wear behavior that qualifies them as ideal solid lubricating coatings. Both exhibit friction coefficients of 0.05 or less in dry air; in load-dependent friction tests, both coatings show interfacial shear strengths around 25 MPa in dry air. Both can have lifetimes of the orders of millions of cycles even though the coatings are one micrometer or less thick. However, their tribological behavior could not have been predicted based on common understanding of solid lubricants. The lubricity of MoS@sub 2@ is associated with easy shear of the basal planes, yet the MoSx-based coatings are amorphous. Often called diamond like carbon, a-C:H is a very hard material (12 - 16 GPa), with no easy shear planes. These discrepancies - between materials properties and tribological properties - can be reconciled by recognizing the role that third bodies play in the friction and wear of the two coatings. The low friction is associated with a film that transfers from the coating to the (counterface) slider and the velocity accommodation mode - interfacial sliding - between the transfer film and the parent coating. The higher friction coefficients of both in humid air is also explained by interfacial sliding and attributable to a higher interfacial shear strength in the presence of humidity. Earlier studies demonstrated that third body recycling from reservoirs contributed to the long life of MoS@sub 2@ coatings, and recent in situ tribometry studies also suggest ways in which the transfer film contributes to long life of diamond-like carbon, as well. Thus, both the friction behavior and the long life of these two otherwise different coating materials can be accounted for by third body effects on sliding contacts.

10:00am **SE-TuM6 In-situ Quantitative Nano-scale Metrology of Thin Coatings***, **N. Gitis**, A. Daugela, A.K. Sikder, M. Vinogradov, A. Meyman,* Center for Tribology, Inc.

Quantitative nano-metrology tools have become a standard in semiconductor, data storage and other hi-tech industries where products are tested for coating properties. Though it is critical to characterize advanced thin films and coatings, todayâ?Ts off-line nanoscale metrology tools can capture only limited number of manufacturing process stages. A quantitative nano/micro-instrument mod. UNMT with both SPM and optical microscope imaging integrated into it was developed to characterize mechanical properties of thin films and coatings and monitor their changes during indentation, scratching, reciprocating, rotating and other tribology tests. Both the materials properties and surface topography can be assessed at various stages of the tests. A 5-um thick copper layer on a silicon wafer was tested for changes in material properties during tribology test. Integrated SPM type imaging and nano-indentation tests revealed changes in elastic modulus, hardness and surface topography at nanometer scale. Dynamics of the copper layer hardening was recorded at several hundreds time steps during the entire tribology test.

10:20am **SE-TuM7 Effect of Impurities and Deposition Condition on the Mechanical Properties of Superhard Nanocomposites with High Thermal Stability***, **S. Veprek**,* Technical University Munich, Germany **INVITED**

Nano-Sized and Nano-Structured materials represent the leading edge of the research and technological development in many different areas from inorganic to biological ones. This paper will address the preparation and properties of superhard nanocomposites with a high thermal stability and an unusual combination of mechanical properties which were developed on the basis of our generic design concept that was published in 1995. These superhard nanocomposites were recently introduced into a large-scale industrial production. Because many researchers have recently claimed a lack of reproducibility of our results, the emphasis of my lecture will be on the deposition conditions needed for a reproducible preparation of these nanocomposites. A special attention will be paid to the detrimental role of impurities in these and other nano-structured coatings. It will be shown that minor oxygen impurities of @>=@0.4 at. % are the most probably reason why a number of researcher were unable to reproduce our data.

11:00am **SE-TuM9 Development of Hybrid Deposition Techniques for Nanocomposite Coating Growth***, **A.A. Voevodin**, J.G. Jones, J.S. Zabinski,* Air Force Research Laboratory

Development of hybrid processes, combining filtered vacuum arc deposition, magnetron, sputtering, and laser ablation for synthesis of functionally gradient and nanocomposite materials are discussed. Hybrid techniques facilitate a high degree of structural control and allow growth of nanostructured materials at low temperature by mixing plasma streams from various sources. Special attention was given to process instrumentation for plasma chemistry and energy control. Spectroscopic, imaging and time of flight analysis techniques are discussed. Interesting plasma interactions were found in a hybrid of laser ablation and ion beam deposition, where short-lived interactions between two plasma sources were explored to produce alumina oxinitride films. In addition, studies of a combination of laser ablation with magnetron sputtering (MSPLD) are presented. In this hybrid process, highly energetic plasma plumes from laser ablation were intersected with a magnetron-generated plasma containing sputtered metal atoms. Another hybrid process combined filtered vacuum arc and magnetron sputtering. All processes were tuned to produce advanced tribological coatings for wear protection of engineering components, combining metals, oxides, carbides, and dichalcogenides into various nanocomposite coating designs.

11:20am **SE-TuM10 Growth and Characterization of Zirconium Nitride/Inconel Nanocomposite Structures***, **S.M. Aouadi**, M. Debessai,* Southern Illinois University*; J. Xu, S.R. Mishra,* University of Memphis*; D.M. Mihut, S.L. Rohde,* University of Nebraska

This paper reports on the first study of the physical, chemical, and mechanical properties of reactively sputtered zirconium nitride/inconel nanocomposite films as a function of chemical composition, and substrate bias. Several sets of samples were deposited on Si(111) substrates at room temperature with bias voltages in the -45 to -160 V range. The chemical composition was deduced from X-ray photoelectron spectroscopy and energy dispersive X-ray fluorescence measurements, and was found to be influenced by the sputtering power and substrate bias. The phase composition and the grain size were determined using X-ray diffraction. The grain size was found to decrease with the increase in power to the inconel gun. The optical constants were measured using spectroscopic ellipsometry. A correlation between film structure/composition and optical constants was established. The hardness and elastic modulus of each sample were measured by nanoindentation. The resistance to plastic deformation, as measured by the ratio H3/E2, was optimized (H3/E2=1.0) with a substrate bias of -100 V. Finally, the tribological behavior of these films was studied using a nanowear tester. Nanowear results correlated well with the resistance to plastic deformation deduced from nanoindentation measurements.

11:40am **SE-TuM11 Microstructure and Properties of Ti-Al-Si-N Coatings Prepared by r.f.-Reactive Sputtering in Facing Targets-type Sputtering (FTS) System***, **M. Nose**,* Takaoka National College, Japan*; W.A. Chiou,* Univ. of California at Irvine*; H. Suzuki,* Toyama Univ., Japan*; E. Honbo,* Toyama Industrial Research Center, Japan*; S. Ikeno, H. Anada,* Toyama Univ., Japan*; S. Nogi,* Osaka Univ., Japan

Ti-Al-N films have been widely used in the coating industry as a superior wear protection material in comparison with its predecessor, TiN; however, the discovery of Ti-Si-N nano-composite film (by Veprek et. al. in 1995) has sparked recent interest in the study of quaternary system coatings such as Ti-Al-Si-N. Research on the influence of Si content on the mechanical properties of the quaternary system has been reported, however, the studies of microstructure and properties of Ti-Al-Si-N films containing high Al content are scarce. The effect of Si concentration on the microstructure and on high aluminum-content systems (such as (Ti@sub0.5@A1@sub0.5@)@sub50@-N@sub50@ film), remain unclear. Thin Ti-Al-Si-N films were synthesized by r.f. reactive sputtering in a facing target-type sputter (FTS) system on the hight speed steel substrates. A pair of composite targets consisting of a Ti@sub50@-Al@sub50@ plate and Si chips was used. During the deposition the substrate was heated from room temperature up to 300° C. The crystallite size of the deposited film without bias voltage decreased from 14 nm to 7 nm with the increase of Si content up to about 7 at. %. XRD patterns of Ti-Al-Si-N films suggested two phases, the cubic B1 NaCl type structure and an amorphous phase, were presented in the film. XPS analysis exhibited a peak that corresponded to the Si@sub3@N@sub4@ phase. TEM investigation of (Ti@sub48@-Al@sub0.48@-Si@sub0.04@)@sub50@-N@sub50@ films revealed a nano-column structure. The nano-column structure has a long aspect ratio ranging from 3 to 10 with an average around 7 to 9. Without applying substrate bias, the hardness of the films increased from 35 GPa for Ti-Al-N films, reaching a maximum of 38GPa for Ti-Al-Si-N films containing approx. 4 at. % Si. Based on thermal-gravity measurement by oxidation of films at 900° C in the air, the oxidation ratio of the Ti-Al-Si-N films was only a quarter of that in Ti-Al-N films. These special characteristics of the Ti-Al-Si-N films are potential results from the formation of an amorphous Si@sub3@N@sub4@ phase.

Surface Science

Room 210B - Session SS1-TuM

Catalytic Reactions: The Role of Surface Steps and Structure

Moderator: G.B. Fisher, Delphi Research Labs

8:20am **SS1-TuM1 Surface Reactions and Catalysis**, ***G.A. Somorjai,*** Lawrece Berkeley National Laboratory and University of California, Berkeley **INVITED**

New techniques developed over the past ten years permit the monitoring of surface structure and surface composition at high pressures and at solid-liquid interfaces. Among them sum frequency generation (SFG) vibrational spectroscopy and high pressure scanning tunneling microscopy high pressure (STM) have been used in my laboratory to monitor catalyst surfaces during reaction. C-H bond activation was studied using C6 hydrocarbons, and reaction intermediates that produce branched isomers or benzene on platinum (111) surfaces (both components of high-octane gasoline) were detected by SFG. High pressure STM reveals surface mobility of adsorbates during catalytic hydrogenation and active metal surfaces. Poisoning the reaction by the coadsorption of carbon monoxide also produces ordered surface structures. These studies indicate that diffusional mobility of adsorbates correlates with catalytic activity.

9:00am **SS1-TuM3 The CO-oxidation Reaction on Pt(111) and Pt(553): The Role of Steps**, ***J.N. Andersen,*** *J. Gustafson, M. Borg, A. Mikkelsen, J. Weissenrieder, E. Lundgren,* Lund University, Sweden*; W.X. Li, B. Hammer,* Aarhus University, Denmark

Catalytic materials often consist of small metallic particles dispersed on a support. The large proportion of undercoordinated (edge) atoms on such small particles may substantially influence the catalytic activity. Experimentally, the influence of undercoordinated atoms may be scrutinized by studying vicinal surfaces using methods that allow separate monitoring of what happens at the steps. Theoretically, the effects may be simulated using density functional theory (DFT) based total energy calculations. We present experimental and theoretical results for the adsorption of O and CO as well as for the CO-oxidation on Pt(111) and Pt(553) surfaces using high resolution core level spectroscopy and DFT based slab calculations. The results directly demonstrate that Pt(553) is more efficient in oxidizing CO than Pt(111), and allow us to obtain a very detailed picture of the microscopic processes responsible for this increased reactivity. A crucial result is the experimental and theoretical demonstration that CO molecules adsorbed at steps and on terraces, respectively, can be distinguished via their C 1s binding energies. These C1s fingerprints allow us to follow in a very detailed manner where CO molecules adsorb and react with preadsorbed oxygen. We study the CO oxidation by preadsorbing oxygen at 310K followed either by exposure to CO at the chosen reaction temperature or by annealing at the chosen reaction temperature of a CO overlayer adsorbed at low temperature. The results show that the CO2 production is more efficient on Pt(553) than on Pt(111). By utilizing the mentioned core level fingerprints, we show directly that the increased oxidation rate on Pt(553) is due to that the oxygen adsorbed in the proximity of steps is more reactive than oxygen adsorbed on the terraces. Comparison to theoretical results from DFT proves vital in fully understanding these experimental results and constructing the detailed microscopic model.

9:20am **SS1-TuM4 Controlling the Catalytic Reactivity and Selectivity of Ni Surfaces by Step Blocking**, ***R.T. Vang,*** University of Aarhus, Denmark*; K. Honkala,* Technical University of Denmark*; S. Dahl,* Haldor Topsøe A/S, Denmark*; E.K. Vestergaard, J. Schnadt, E. Lægsgaard,* University of Aarhus, Denmark*; B.S. Clausen,* Haldor Topsøe A/S, Denmark*; J.K. Nørskov,* Technical University of Denmark*; F. Besenbacher,* University of Aarhus, Denmark

Step or defect sites have been shown to dominate the reactivity of catalytic surfaces for the dissociation of a number of diatomic molecules, but so far no studies have addressed the influence of steps in the decomposition of more complex molecules. In most catalytic processes involving hydrocarbon molecules, selectivity (between, e. g., C-H and C-C bond breaking) is crucial for the overall efficiency of the catalyst. In this study we have used STM and DFT calculations to investigate the dissociative adsorption of a simple molecule, CO, as well as a more complex molecule, ethylene (C@sub 2@H@sub 4@), on Ni(111). The STM studies reveal that both molecules decompose at the step edges at a much higher rate than on the (111) facets. These observations are supported by DFT calculations showing a much lower activation barrier for decomposition at a step site compared to a terrace site. Furthermore, the steps are shown to have a crucial influence on the selectivity of the Ni(111) surface towards ethylene decomposition, in the sense that the step effect is much more pronounced for C-C bond breaking than for C-H bond breaking. We also demonstrate how we can control the number of active step sites and thus the reactivity by depositing small amounts of Ag, which from STM studies are shown to block all the step sites on the Ni(111) surface. Finally we exploit this new principle of step control by synthesizing a new high-surface area supported NiAg alloy catalyst. We show in flow reactor tests that the NiAg catalyst has a much lower activity for ethane hydrogenolysis than a similar Ni catalyst, thus confirming that we can block C-C bond breaking by step control.

9:40am **SS1-TuM5 High Pressure Scanning Tunneling Microscopy Study on CO Poisoning of Ethylene Hydrogenation on Metal Single Crystals**, *G.A. Somorjai,* University of California, Berkeley*;* ***D.C. Tang***[1]*, M. Salmeron,* Lawrence Berkeley National Laboratory*; K.S. Hwang,* University of California, Berkeley

The nature of catalyst poisoning under reaction conditions is an important question in catalysis science@footnote 1@@super ,@@footnote 2@. During a reaction the catalyst surface is covered with a dense layer of adsorbates in equilibrium with the gas phase. This layer consists of reactants, inactive spectator molecules, and active poisoning adsorbates@footnote 3@. For the reaction to occur the surface should remain flexible, atomic rearrangements should be possible, and adsorbate mobility should be high enough so that favorable adsorption sites can be accessed. Using a high pressure scanning tunneling microscope we monitored the co-adsorption of hydrogen, ethylene and carbon dioxide on rhodium (111) and platinum(111) crystal faces in the mTorr pressure range at 300 K in equilibrium with the gas phase. We show that poisoning occurs when surface mobility is suppressed and the adsorbate species become locked into static ordered structures. During the catalytic hydrogenation of ethylene to ethane in the absence of CO the metal surfaces are covered by an adsorbate layer that is very mobile on the time scale of STM imaging. We found that the addition of CO poisons the hydrogenation reaction and induces ordered structures on the single crystal surfaces. Several ordered structures were observed upon CO addition to the surfaces pre-covered with hydrogen and ethylene: domains of c(4 x 2)-CO+C@sub 2@H@sub 3@, previously unobserved (4 x 2)-CO+3C@sub 2@H@sub 3@, and (2 x 2)-3CO on Rh(111), and a (@sr@19 x @sr@19)R23.4° on Pt(111). A mechanism for CO poisoning of ethylene hydrogenation on the metal single crystals was proposed, in which CO blocks surface metal sites and reduces adsorbate mobility to limit adsorption and reaction rate of ethylene and hydrogen. @FootnoteText@ @footnote 1@ Bartholomew, C. H. App. Catal. A 212, 17-60 (2001).@footnote 2@ Kumbilieva, K., Kiperman, S. L. & Petrov, L. Kinet. Catal. 36, 73-79 (1995).@footnote 3@ Zaera, F. Prog. Surf. Sci. 69, 1-98 (2001).

10:00am **SS1-TuM6 Iridium (210): Nanoscale Faceting and Structure-sensitivity of Surface Reactions**, ***I. Ermanoski,*** *W. Chen, T.E. Madey,* Rutgers University

The stability of the atomically rough fcc Ir(210) surface depends on its cleanliness. The clean surface is planar and unreconstructed after heating in UHV up to 2100K. The oxygen-covered surface is, however, structurally unstable, and undergoes a dramatic faceting transformation: Nanometer-sized pyramids exposing {311} and (110) faces are formed upon deposition

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

of more than 0.5 monolayers of oxygen and annealing to 600K, completely replacing the original planar surface. The oxygen-covered faceted surface reversibly reverts to planar at ~ 900K. LEED and STM experiments show that pyramid sizes increase with annealing temperature, and can reach ~25nm. This growth does not have an effect on the orientation of the facets. The complete thermal desorption of oxygen from iridium requires a temperature of ~1400K, and causes a complete destruction of the faceted structure. Nevertheless, by using catalytic CO oxidation (at ~550K) and reaction of H2 to form H2O (at ~400K), we have been able to routinely prepare a clean faceted surface in situ. Owing to the ability to prepare clean surfaces of different nano-scale structure (planar, faceted, varying facet sizes) from Ir(210), we have found it to be an excellent substrate for studying the kinetics of surface chemical reactions that depend on the surface structure. Our temperature programmed desorption (TPD) experiments show that thermal decomposition of acetylene, hydrogen recombinative desorption and ammonia decomposition all exhibit structure sensitivity, and proceed differently on the planar and faceted surfaces. Furthermore, differences are observed in reactions on clean faceted surfaces with different average facet sizes, showing that particle-size effects also play an important role in these reactions.

10:20am **SS1-TuM7 Kinetics of Co Oxidation Catalyzed by Supported Iridium Particles in a Wide Pressure Range***, **M.M. Sushchikh**, E.W. McFarland,* University of California, Santa Barbara

Recent work in ultra-high vacuum (UHV) has demonstrated kinetic hysteresis in the CO oxidation reaction on single crystal iridium surfaces@footnote 1@,@footnote 2@; the reaction rate variation in CO and O@sub 2@ partial pressures varied depending upon the initial partial pressure. The phenomena observed were explained using a Langmuir-Hinshelwood mechanism. We have investigated the phenomena at elevated pressures on a supported Ir catalyst to test the validity of the model scaled more than 9 orders of magnitude in pressure. It is expected that sticking coefficients at the high surface coverages are not equal to those at lower coverages and as the pressure approaches atmospheric, kinetic phase transitions are affected by changes in the gas composition. Furthermore, on the supported metal particulate catalyst heat transfer effects are more complex. The rate of CO@sub 2@ formation on Ir as a function of reactant pressures (up to 1 atm) was monitored and excellent agreement was found with the UHV experiments. @FootnoteText@ @footnote 1@ S.Wehner, F.Baumann, M.Ruckdeschel, J.Küppers, J.Chem.Phys., 119(13)(2003)6823.@footnote 2@ S.Wehner, F.Baumann, J.Küppers, Chem.Phys.Lett., 370(2003)126.

10:40am **SS1-TuM8 High Pressure Methane Activation on Platinum Single Crystal Surfaces***, **A.L. Marsh**, R.M. Rioux, J.S. Gaughn,* University of California, Berkeley*; G.A. Somorjai,* University of California, Berkeley and Lawrence Berkeley National Laboratory

The interest in alternative sources of energy has generated research on the conversion of hydrocarbons such as methane into hydrogen for both stationary and mobile fuel cell applications. To optimize the processes for the conversion of methane into hydrogen using platinum catalysts, reaction mechanisms must be characterized at a molecular-level. For that reason, we have characterized the high-pressure (up to 40 Torr) activation of methane on platinum single crystal surfaces using infrared-visible sum frequency generation (IR-VIS SFG) spectroscopy and Auger electron spectroscopy (AES). At low temperatures (300 K) and high pressures (1 Torr), methane is activated to form a number of different dehydrogenated intermediates on the Pt(111) surface. The extent of dehydrogenation increases with increasing temperature and pressure. In addition, the amount of carbon deposited on the surface increases with increasing temperature and pressure. Comparisons are made with molecular beam and high pressure experiments on other metal single crystal surfaces to develop a detailed mechanistic picture of the activation of methane at high pressures on platinum catalyst surfaces.

11:00am **SS1-TuM9 Nanoporous Pd Films Grown Via Ballistic Deposition: Structural And Catalytic Properties***, **J. Kim**, Z. Dohnálek, B.D. Kay,* Pacific Northwest National Laboratory

Hydrogenation of ethylene was studied on dense and nanoporous Pd films using molecular beams and temperature programmed desorption (TPD). Porous films were deposited on a Mo(100) substrate at temperatures ranging from 22 to 300 K. Due to limited surface mobility at such low temperatures, the growth is dictated by a ballistic deposition mechanism. The adsorption properties of the films were characterized as a function of Pd deposition angle as well as growth and post-annealing temperatures using N@sub 2@ physisorption. The highest surface area of ~ 80 m@super 2@/g was observed for films grown at 85° and 22 K. Upon annealing to 300 K, the films lose ~40 % of their area, further annealing to 500 K leads to complete densification. Reactivity studies show that nanoporous Pd, covered with H and subsequently saturated with ethylene at 22 K, is highly efficient catalyst for ethylene hydrogenation. This is in sharp contrast with dense Pd films where only trace amounts of ethane were observed. As seen from the reaction yields on films preannealed to various temperatures, the number of catalytically active sites decreases faster than the area of the films. Additionally, cycling of the ethylene hydrogenation reaction also leads to a decrease of ethane production due to poisoning of the active sites.

11:20am **SS1-TuM10 Novel NO Adsorption States on Pd (111) at Elevated Pressures: Irreversibility of the Effects of Temperature and Pressure on Heterogeneous Catalytic Systems***, **E. Ozensoy**[1],* Texas A&M University*; Ch. Hess,* Fritz-Haber-Institut der Max-Planck-Gesellschaft,Germany*; C. Yi,* Texas A&M University*; D. Loffreda,* Institut de Recherches sur la Catalyse, Centre National de la Recherche Scientifique, France*; D.W. Goodman,* Texas A&M Univeristy

NO adsorption states on Pd (111) single crystal model catalyst surface were investigated using in-situ polarization modulation infrared reflection absorption spectroscopy (PM-IRAS) and density functional theory (DFT) calculations within 10@super -9@ - 400 mbar and 25-600 K. Vibrational spectroscopic data and DFT calculations indicate that besides the well-known monomeric NO adsorption states, a novel high-coverage monomeric adsorption state was observed at elevated pressures which was identified to have a (3x3)-7NO structure. NO-dimer states were also determined to exist under both ultra high vacuum (UHV) and elevated pressure conditions, however the nature of the NO-dimers that are formed at low and high pressures were found to be different in terms of their surface coverage, the strength of their interaction with the Pd (111) surface and the intrinsic N-N bond strength. In addition, the formation of dinitrosyls at @theta@@sub NO@ > 0.778 ML was also observed and found to take place only at elevated pressure and temperature conditions suggesting that not all of the thermodynamic equilibrium states at elevated temperatures and pressures are kinetically available at low temperatures and pressures for NO/Pd (111), emphasizing the danger of extrapolating the results of traditional surface scientific experiments performed under to UHV conditions to elevated pressure and temperature cases where the behavior of the system can show remarkable deviations from the expectations.

Surface Science
Room 210C - Session SS2-TuM
Self Assembled Monolayers

Moderator: M. Grunze, University of Heidelberg, Germany

8:20am **SS2-TuM1 Vapor-Phase Adsorption Kinetics of 1-Decene on Hydrogenated Si(111)***, **M.R. Kosuri**, H. Gerung, Q. Li,* University of New Mexico*; S.M. Han,* University of New Mexico, U. S. A.

We have investigated in situ and in real time vapor-phase self-assembly of 1-decene on hydrogenated Si(111), using attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIRS). The p- and s-polarized IR absorbance of Si-H vibrational mode at 2084 cm@super -1@ strongly supports that the Si(111) surface is terminated with monohydrides prior to 1-decene exposure. The adsorption of 1-decene on hydrogenated Si(111) results in a decane terminated hydrophobic surface, indicated by the sessile-drop water contact angle. X-ray photoelectron spectroscopy is additionally used to determine the temperature dependence on self-assembled monolayer (SAM) formation. The decane SAMs prepared at 80 to 200 °C show an identical saturation surface coverage. The absolute surface coverage, calculated from the IR absorbance of C-H stretching vibrational modes near 2900 cm@super -1@ saturates at 4.3x10@super 14@ cm@super -2@, which translates to 55 % of surface Si atom density. The fractional surface coverage of decane indicates that 1-decene adsorption is a two-step process following a 1st order Langmuir isotherm: (1) fast adsorption with an empirical rate constant k@sub 1@ = 4.2x10@super -2@ min@super -1@ and (2) slow adsorption with an empirical rate constant of k@sub 2@ = 1.6x10@super -2@ min@super -1@. The thickness and cant angle of the decane SAM at the saturation coverage are calculated to be 13 Å and 15° from the surface normal,

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

respectively. In this presentation, we will also discuss the stability of decane SAMs against ambient exposure over time.

8:40am **SS2-TuM2 Molecular Monolayers on Single-Crystal and Nanocrystalline Diamond Surfaces*, B.M. Nichols,*** University of Wisconsin-Madison*; J.E. Butler, J.N. Russell, Jr.,* Naval Research Laboratory*; R.J. Hamers,* University of Wisconsin-Madison

The chemical stability and electronic properties of diamond make it an attractive substrate for chemical and biological sensing. Recent studies have demonstrated the ability to covalently functionalize nanocrystalline diamond surfaces with molecules bearing a terminal vinyl (C=C) group via a photochemical process under ambient conditions. Here, we report studies of the properties of monolayer films formed on single-crystal diamond(111) and on polycrystalline diamond thin films by this process. XPS measurements on diamond(111) surfaces functionalized with molecules bearing a vinyl group at one end and a fluorine-protected amine group at the other show that the F/C ratio saturates after ~12 hours of reaction, suggesting a self-terminating monolayer. To prove that the molecules are aligned vertically on the surface, we measured the angular dependence of the apparent F/C ratio; this measurement shows that the F atoms are preferentially located at the exposed surface. We find that single-crystal and nanocrystalline samples have similar reaction rates, thereby eliminating the potential role of grain boundaries or graphitic impurities. To characterize the electronic properties, we measured valence-band photoemission spectra and work functions of clean, H-terminated, and molecularly-functionalized diamond(111) surfaces. Our results indicate that the molecularly-modified samples have work functions comparable to the annealed, clean diamond(111) surface, and substantially higher than the H-terminated sample. We will discuss these results and the relationship between the chemical structure, electronic structure, and photochemical functionalization of diamond surfaces.

9:00am **SS2-TuM3 High Resolution Mapping of Compositional Differences and Reactions at Buried Interfaces by Electric Force Microscopy***, H. Takano,* University of Pennsylvania*; G. Edwards, A.J. Bergren, J. Driskell, R.J. Lipert,* ***M.D. Porter,*** Iowa State University **INVITED**

The ability to interrogate the chemical composition of organic films is of vast importance to many areas in interfacial and surface science (e.g., electrocatalysis, corrosion inhibition, organic electronic devices, and biocompatability). This presentation describes two sets of results that demonstrate the ability of electric force microscopy (EFM) to map compositional differences of organic monolayers buried under thick polymer films. The first example examines the compositional mapping of organic monolayers buried under an ~430 nm film of polystyrene. The underlying adlayer was patterned onto a gold surface using the microcontact printing of CH3(CH2)16SH followed by solution deposition of HO(CH2)16SH. This procedure results in alternating domains of different terminal groups. Results show that the imaging mechanism exhibits sufficient contrast to function as a mapping methodology for buried functional groups. The second example presents the results from monitoring photochemical reactions of polymeric films deposited on organic monolayer-covered metal substrates. UV-light was irradiated on the polymer/monolayer/metal composites through a photomask, resulting in alternating domains. These findings show not only that EFM can distinguish the domains of reacted and non-reacted portions, but also that EFM can provide sufficient contrast as a subsurface mapping technique. Issues related to the imaging mechanism are also examined. Models that explore the fundamental basis of this capability are also discussed.

9:40am **SS2-TuM5 Chemical Engineering of GaAs Surfaces with Aromatic Self-Assembled Monolayers*, M. Zharnikov*,** *A. Shaporenko,* Universität Heidelberg, Germany*; K. Adlkofer,* Technische Universität München, Germany*; A. Ulman,* Polytechnic University*; M. Tanaka,* Technische Universität München, Germany*; M. Grunze,* Universität Heidelberg, Germany

Stochiometric GaAs (100) surfaces were functionalized with monolayers of non-substituted and substituted thiol-derived aromatic compounds and the engineered surfaces were studied by several complementary experimental techniques including synchrotron-based high resolution x-ray photoelectron spectroscopy and near edge x-ray absorption fine structure spectroscopy. The aromatic molecules were found to form well ordered and densely packed self-assembled monolayer on these substrates. The attachment to the substrate occurs over the thiolate headgroup while the intact aromatic chains have an upright orientation with an average tilt angle of about 30°. The functionalization of GaAs was found to prevent an oxidation and contamination of the substrate, keeping the GaAs surface in a pristine state. In addition, the wetting properties of this surface could be controlled by the selection of a suitable substitution, e.g. methyl or hydroxy group. The surface engineering of GaAs with functionalized aromatic monolayers can provide a crucial link for combining GaAs-based heterostructures and devices with bio-organic molecular assemblies.

10:00am **SS2-TuM6 Self Assembled Monolayers of Arenethiol Molecules on Cu(111)*, K. Wong*,** *K.-Y. Kwon, B.V. Rao, A. Liu, L. Bartels,* University of California, Riverside

The utility of the thiol group on anchoring organic molecules to metal surfaces has been widely recognized. The thiol group makes sufficiently strong bonds with the metal substrate that stable monolayers are formed spontaneously even at room temperature in a solution environment. At low coverages and under ultra-high vacuum conditions isolated thiols exhibit significant surface mobility even at temperatures as low as 80K. We have studied monolayers of thiolphenol (TP) molecules and several halogen substituted para-X-TP derivates (where X is Br, Cl or F) at various coverages. All TPs adsorb with the benzene ring parallel to the surface and do not tilt to a vertical orientation as long as there is sufficient surface area available to accommodate all adsorbed molecules in a horizontal fashion. At such coverages we find a pronounced dependence of the ability of the TPs to form ordered films on the nature of their substitution. The most remarkable differences were found at incomplete coverage where the molecules have space to rearrange themselves into the optimal surface conformation and are not exposed to lateral stress. X-TP molecules form patterns of various degrees of complexity: Br-TP forms a simple (3x4) structure with one molecule per unit cell. Cl-TP films are made up of slightly more complicated unit cells involving two neighboring molecules whose sulfur atoms are located in different (hcp and fcc) Cu(111) hollow sites. F-TP molecule self assemble into a (8x8)R19@super o@ honeycomb pattern consisting of seven molecules per unit cell. Unsubstituted TP and pentafluoro-TP do not form any extended ordered patterns. This suggests that differences in the chemical properties between the para- and the meta-/ortho- substituents of TPs play a crucial role in the pattern formation process. We present a model based on quadrupolar intermolecular interaction to account for these observations.

10:20am **SS2-TuM7 Fabricating Self-Assembled Monolayers of Selenolates on Noble Metal Substrates*, A. Shaporenko,*** Universität Heidelberg, Germany*; A. Ulman,* Polytechnic University*; A. Terfort,* Universität Hamburg, Germany*; M. Grunze, M. Zharnikov,* Universität Heidelberg, Germany

Self-assembled monolayers (SAMs) of selenolates can be considered as an alternative to thiolates for fabricating SAMs on noble metal surfaces. To prove this approach, we applied a standard immersion procedure to prepare SAMs from several aliphatic and aromatic selenide and diselenide compounds on gold and silver substrates. The resulting films were characterized by several complementary experimental techniques including infrared refection-absorption spectroscopy (IRRAS), synchrotron based high-resolution X-ray photoelectron spectroscopy (HRXPS), near edge X-ray absorption fine structure spectroscopy, and contact angle measurements. The results suggest a dissotiative mode of monolayer formation from diselenide compounds on both gold and silver. However, in the case of long chain alkylselenides and dialkylselenides, no high quality films were formed. In the case of short chain alkylselenides, semifluorinated alkylselenides, and biphenylselenides, well-defined and densely packed SAMs were fabricated. Only one selenium species, namely selenolate was found in all above-mentioned films on the basis of the Se3d HRXPS spectra. Distinct C1s photoemission peaks were observed and related to well-defined aliphatic or aromatic chain. Characteristic IR absorption bands and X-ray absorption resonances corresponding to intact molecular chains of definite conformation were observed. The information on molecular orientation and packing density was derived.

10:40am **SS2-TuM8 Interface Electronic Structure of Thiol Terminated Molecules on Metals*, A.N. Caruso*,** *L.G. Wang, E.Y. Tsymbal, S.S. Jaswal, P.A. Dowben,* University of Nebraska

Thiol terminated molecules may be useful to both molecular electronic and spintronic applications. The orientation and electronic properties of biphenyldimethyldithiol (S-CH@sub 2@-C@sub 6@H@sub 4@-C@sub 6@H@sub 4@-CH@sub 2@-S) adsorbed on Au(111) and polycrystalline cobalt are identified from combined polarization dependent photoemission and inverse photoemission. The stable orientation, bonding site and electronic properties of methylthiolate (S-CH@sub 3@) adsorbed on Au(111) and Co(0001) are found by density functional calculations. Both experiment and theory show a stronger bonding to cobalt over gold surfaces for both thiol terminated molecules. Calculated charge transfer with the substrates to and from the sulfur further confirms bonding and reasoning behind the experimentally found highest occupied to lowest unoccupied molecular orbital gap offset from the Fermi level. Calculations also show that the three-coordinated fcc and hcp hollow sites are most stable for methylthiolate adsorption.

11:00am **SS2-TuM9 Designing Self-assembled Monolayers (SAM) of Thiols: A Study on Lattice Mismatch**, *P. Cyganik, **M. Buck**,* St Andrews University, UK*; C. Woell,* Ruhr-Universitaet Bochum, Germany

Applications of self-assembled monolayers (SAM) of thiols in, e.g., molecular electronics or electrochemistry are crucially dependent on the extent to which their properties can be controlled. Besides the control of the molecular electronic properties, controlling the structure, i.e., defects and crystallinity, is an issue of equal importance. As for any adsorbate system tailoring of SAMs has to address mismatch between molecular and substrate lattices. Surprisingly, this aspect which is of fundamental importance toward a controlled design of thiol SAMs has received very little attention. The talk presents STM studies on biphenyl based thiols which are characterized by an alkane spacer between the sulphur head group and the aromatic moiety. Within a homologue series of these biphenyl thiols with the spacer varying from 0 to 6 methylene units, intermolecular interactions, molecular orientation, and, thus, packing of the molecules are substantially changing. Contrast variations in scanning tunneling microscopy images reveal lattice mismatch. The way mismatch is accomodated depends strongly on the alkane spacer and, therefore, the achievable structural perfection is varying across the homologue series. The results suggest that a flexible spacer acts as a buffer layer which can accomodate mismatch between the lattice of aromatic moieties and the substrate lattice.

11:20am **SS2-TuM10 Sulfur-induced Nano-restructuring of the Au(111) Surface: A Real-time STM Study**, ***M.M. Biener,*** Harvard University*; J. Biener,* Lawrence Livermore National Laboratory*; D. Pinnaduwage, C.M. Friend,* Harvard University

The interaction of sulphur with gold surfaces has attracted considerable interest due to numerous technological applications such as the formation of self-assembled monolayers (SAMs), corrosion inhibition, and sensors. In this work, the interaction of sulfur with Au(111) was studied by real-time scanning tunnelling microscopy (STM) using sulfur dioxide as a source of sulfur. A small fraction of the impinging sulfur dioxide molecules deposit sulphur on the surface. Up to a coverage of ~0.3 ML sulfur forms an ordered adlayer. With further increasing S coverage we observe the formation of a two-dimensional AuS overlayer exhibiting short range order. Gold atoms are removed from the surface and are incorporated into the growing gold sulfide resulting in pit formation. This gold sulfide layer is stable up to ~500 K where it develops long-range order and exhibits a complex Low Energy Electron Diffraction (LEED) pattern. We will present nano-scale, time-resolved movies capturing the sulphur induced restructuring of the Au(111) surface.

11:40am **SS2-TuM11 Comparative UHV-STM Study of Adsorption Structures Formed from a Family of Oligo(phenylene ethynylene)s on Au(111)**, *L. Petersen, C. Busse, S. Terkelsen, **T.R. Linderoth**, M. Nielsen, K.V. Gothelf, F. Besenbacher,* University of Aarhus, Denmark

To realize the goal of functional structures formed by molecular self-assembly, systematic studies of factors directing the assembly process are required. Using UHV-STM we have performed a comparative study of adsorption structures formed by a family of structurally different, but chemically similar, organic molecules adsorbed on the Au(111) surface. The molecules consist of a central benzene ring with three or two acetylene spokes (para, meta, or ortho) leading to highly conjugated pi-systems of three-spoke, linear, bent, or v-shaped molecular geometry. Each spoke terminates in a tert-butyl substituted salicylaldehyde moiety. Upon adsorption at room temperature (and imaging at ~150 K to reduce molecular mobility), a variety of close-packed phases are observed, most of which can be rationalized by a common motif of molecules adsorbed with their backbone parallel to the surface and with optimized intermolecular side-to-side interaction, most likely through van der Waals coupling. Interesting exceptions to this picture are the linear molecules, which in addition form a more open nano-grid type structure thought to be dominated by intermolecular hydrogen bonding, and the v-shaped molecules where a reduced footprint indicates non-planar adsorption geometry. The described results constitute a platform for ongoing experiments where (i) similar molecules with systematically altered functional moieties are used, e.g. disabling or further encouraging intermolecular hydrogen bond formation, (ii) structures formed through co-adsorption with transition metals (Ni,Fe) are investigated, and (iii) intermolecular covalent cross-linking is induced through co-adsorption with reactive diamines.

Thin Films
Room 303C - Session TF1-TuM
Thin Films on Flexible and Polymer Substrates

Moderator: H. Kim, IBM Research

8:20am **TF1-TuM1 Mechanisms of Vapor Permeation Through Multilayer Thin-Films**, ***G.L. Graff**, P.E. Burrows, R.E. Williford,* Pacific Northwest National Laboratory **INVITED**

Multi-layer, thin-film organic/inorganic composite barrier layers can achieve water vapor permeation rates (WVTR) of <10@super-5@ g/m@super2@/day at 25°C/40%RH on polyethylene terephthalate. Using both transient and steady-state vapor permeation measurements combined with classical Fickian diffusion models, we determine the mechanism of vapor permeation through such barrier structures and show the importance of an extremely long effective path length for the diffusing gas. We show that the barrier performance obtained is dominated by lag-time (transient) effects, rather than equilibrium diffusion. The implications for further improvement of flexible thin film vapor barriers are discussed.

9:00am **TF1-TuM3 Multi-layered ITO and SiO@sub 2@ Thin Films Deposited on Plastic Substrates by Vacuum Arc Plasma Evaporation**, ***T. Miyata**, Y. Minamino, T. Minami,* Kanazawa Institute of Technology, Japan

Recently, a vacuum arc plasma evaporation (VAPE) method that provides a high rate deposition on large area substrates has been newly developed. This paper describes the preparation of multi-layered structures composed of ITO and SiO@sub 2@ thin films deposited on plastic substrates by the VAPE method. Structures such as ITO/SiO@sub 2@ and ITO/SiO@sub 2@/ITO were prepared for the purpose of improving the optical transmittance of flexible transparent conducting films that exhibit a desirable sheet resistance, e.g., ITO thin films deposited on thick PET films. The ITO and SiO@sub 2@ thin films were prepared on PET substrates by the VAPE method using sintered ITO and fused quartz fragments, respectively, as targets. The film depositions were carried out under the following conditions: substrate, PET (glass used as a monitor); substrate temperature, 100°C; pressure, 0.08 to 1 Pa; Ar and O@sub 2@ gas flow rates, 20 and 0 to 20 sccm; and cathode plasma power, 4.5 to 10 kW. The optical and electrical properties of the ITO thin films were strongly dependent on the deposition conditions. In addition, the optical transmission spectra of the SiO@sub 2@ thin films also were affected by the deposition conditions. By optimizing the deposition conditions, highly transparent and conductive ITO thin films were prepared at 100°C on both PET and glass substrates. The resistivity of ITO thin films increased from 2.9 to 7.8X10@super –4@@ohm@cm as the O@sub 2@ flow rate was increased from 5 to 20 sccm. In addition, SiO@sub 2@ thin films that were prepared on PET substrates under optimized conditions exhibited a high transmittance in the visible region. Using optimized deposition conditions, ITO/SiO@sub 2@ and ITO/SiO@sub 2@/ITO multi-layered structures with a desirable sheet resistance were prepared on PET substrates based on the theoretical calculation. However, the film thickness of the ITO top layer was determined by the desired sheet resistance. In conclusion, transmittance could be successfully improved in transparent and conductive ITO/SiO@sub 2@ and ITO/SiO@sub 2@/ITO multi-layered structures prepared on flexible plastic substrates by the VAPE method.

9:20am **TF1-TuM4 Mechanical Performance of Thin Films in Flexible Displays**, ***J.S. Lewis**, S. Grego, E. Vick, B. Chalamala, D. Temple,* MCNC Research and Development Institute

In flexible organic light emitting diode (OLED) based displays, brittle thin films are typically used as transparent conductors, permeation barriers, and transistor backplanes. The use of brittle materials in flexible displays requires the understanding of the mechanical limitations of the materials and the various display architectures. We discuss the mechanical limitations of indium tin oxide (ITO) as a transparent conductor, and present results for a more mechanically robust multilayer transparent conductor made of a dielectric-metal-dielectric (DMD) stack. The DMD structures show dramatically improved mechanical properties when subjected to bending both as a function of radius of curvature as well as number of cycles to a fixed radius. Organic light emitting devices fabricated on DMD anodes showed improved performance compared with those made on ITO anodes. The mechanical properties of thin film conductors were investigated by monitoring electrical resistance during flexing, but this approach cannot be used in the analysis of the mechanical failure of transparent thin film permeation barriers. We present a novel approach for etching barrier-coated polymer substrates such that film cracking is readily visible under an optical microscope. We report on the bend test results for sputter-deposited SiO@sub x@N@sub y@ barrier films. This work was supported by the Army Research Laboratory (Contract No. DAAD17-01-C-0085).

9:40am **TF1-TuM5 Structural and Mechanical Properties of Dendrimer-mediated Thin Films***, **F.T. Xu**, S.M. Thaler, J.A. Barnard,* University of Pittsburgh

Dendrimers are three-dimensional, globular, highly-branched macromolecules made up of a central core surrounded by repetitive units all enclosed by a terminal group shell. They can be synthesized with highly controllable sizes (they are monodisperse) determined by the core type, extent of branching, and nature of the end groups, in the range from a few to several tens of nm in diameter. Dendrimers also assemble into monolayers on technologically interesting substrates using simple cleaning, dipping, and rinsing procedures. In this condensed monolayer phase dendrimers can act as surfactants mediating the growth of ultra-flat films, and create novel nanomechanical, adhesive, frictional, and tribological behavior. We have recently reported on the dramatically enhanced quality (superior flatness and adhesion) of metal films deposited on dendrimer monolayers@footnote 1@. Different tribological responses are also observed in dendrimer-mediated metal thin films@footnote 2@. To better understand substrate/dendrimer monolayer/adlayer interactions and how they determine the distinct physical, mechanical, and chemical properties of the resulting dendrimer-based nanocomposites, we are examining the structure and nanomechanical response of metal films formed with and without dendrimer mediation by atomic force and force modulation microscopy. @FootnoteText@ @footnote 1@ S.C. Street, A. Rar, J.N. Zhou, W.J. Liu, and J.A. Barnard, Chem. Mater. 13, (2001)3669.@footnote 2@ F.T. Xu, P.P. Ye, M. Curry, J. A. Barnard and S. C. Street, Trib. Lett. 12 (2002)189 .

10:00am **TF1-TuM6 Gas Diffusion Barriers on Polymer Films Using Al@sub 2@O@sub 3@ Atomic Layer Deposition***, **M.D. Groner**, C.A. Wilson, J.D. Ferguson, S.M. George,* University of Colorado*; R.S. McLean, P.F. Carcia,* DuPont CR&D

Polymer substrates are desirable for flexible organic light-emitting diodes (OLEDs). Unfortunately, gas permeability in polymers is high and gas diffusion barriers are needed to reduce H@sub 2@O and O@sub 2@ permeability. For OLEDs, the desired permeability rate for O@sub 2@ is 1 x 10@super -5@ cc/m@super 2@/day. Inorganic films, such as SiO@sub 2@ and Al@sub 2@O@sub 3@, can have extremely low gas diffusion rates and may be excellent gas diffusion barrier candidates if they are continuous and pinhole-free. Low temperature Al@sub 2@O@sub 3@ ALD has been investigated on a variety of polymer films including PET, PMMA, LDPE, PEN, and Kapton(R). Al@sub 2@O@sub 3@ ALD films were deposited at temperatures between 100-175°C and yielded thicknesses between 1-25 nm on the various polymer substrates. Al@sub 2@O@sub 3@ ALD film growth and film properties were characterized using several techniques including quartz crystal microbalance, FTIR spectroscopy and surface profilometry. O@sub 2@ permeability through the polymer films was also quantified using MOCON permeation measurements. O@sub 2@ permeation rates below the MOCON test limit of 1 x 10@super -3@ cc/m@super 2@/day were measured for Al@sub 2@O@sub 3@ ALD films @>=@ 5 nm thick on PEN and Kapton substrates. New testing methods are currently being developed to measure the extremely low O@sub 2@ and H@sub 2@O permeation rates required for OLED packaging. Studies are also characterizing the dependence of gas permeation rates on the Al@sub 2@O@sub 3@ ALD film thickness and growth temperature.

Thin Films
Room 303C - Session TF2-TuM
ALD and Applications

Moderator: H. Kim, IBM Research

10:20am **TF2-TuM7 Atomic Layer Deposition of Tungsten Disulphide Solid Lubricant Coatings***, **T.M. Mayer**, T.W. Scharf, S.V. Prasad, R.S. Goeke, M.T. Dugger,* Sandia National Laboratories

We have developed a new process for the deposition of polycrystalline tungsten disulphide (WS@sub 2@) solid lubricant coatings with monolayer precision by atomic layer deposition. Sequential reactions of WF@sub 6@ and H@sub 2@S in a viscous flow reactor at 1 to 2 torr and 300 to 400°C lead to growth rates of 0.1 to 0.2 nm/cycle. Nucleation of WS@sub 2@ is impeded on SiO@sub 2@ substrates such that no growth is observed even after 200 cycles. However nucleation occurs readily on ZnO and ZnS substrates and growth catalyzed by the presence of small quantities of Zn, which segregates to the surface of the growing film. SEM with EDS, and Raman spectroscopy determined the coating morphology, composition, and crystallinity, respectively. The friction coefficient was determined to be approx. 0.12 as deposited and decreased to approx. 0.04 when the coating was annealed, well within the acceptable range of other solid lubricant coatings like sputtered MoS@sub 2@ and pulsed laser deposited WS@sub 2@, making this material and process attractive for applications in micromachine technology.

10:40am **TF2-TuM8 Molybdenum Atomic Layer Deposition Using MoF@sub 6@ and Si@sub 2@H@sub 6@***, **G.B. Rayner, Jr.**, S.M. George,* University of Colorado

Although many binary materials have been grown using atomic layer deposition (ALD) techniques, the growth of most single-element metals has been difficult. Tungsten (W) ALD has been demonstrated earlier using WF@sub 6@ and Si@sub 2@H@sub 6@ as reactants. In this study, we extend a similar surface chemistry strategy for Mo ALD. Auger electron spectroscopy (AES) was used to monitor the nucleation and growth during Mo ALD on thin SiO@sub 2@ films thermally grown on Si(100) substrates. Using MoF@sub 6@ exposures of 8 x 10@super 5@ L and Si@sub 2@H@sub 6@ exposures of 4 x 10@super 6@ L at 200°C, the Mo ALD was observed by the attenuation of the O(KLL) AES signal and growth of the Mo(MNN) AES signal. Mo ALD nucleation on SiO@sub 2@ required 10-15 MoF@sub 6@/Si@sub 2@H@sub 6@ reactant cycles. The Si(LMM) AES signal oscillated dramatically during the sequential MoF@sub 6@ and Si@sub 2@H@sub 6@ exposures. No Si(LMM) AES signal was observed following the MoF@sub 6@ exposures that deposit MoF@sub x@ surface species. Large Si(LMM) AES signals were monitored after the Si@sub 2@H@sub 6@ exposures that strip off the fluorine and deposit SiH@sub y@F@sub z@ surface species on the growing Mo surface. Mo ALD may be important for the fabrication of Mo/Si Bragg mirrors for extended ultraviolet (EUV) lithography.

11:00am **TF2-TuM9 Atomic Layer Deposition for the Conformal Coating of Nanoporous Materials***, **J.W. Elam**, G. Xiong, C.Y. Han,* Argonne National Laboratory*; J.P. Birrell,* Argonne National Laboratory, U.S.*; G.A. Willing, H.H. Wang, J.N. Hryn, M.J. Pellin,* Argonne National Laboratory

Atomic layer deposition (ALD) utilizes a binary reaction sequence of self-saturating chemical reactions between gaseous precursor molecules and a solid surface to deposit films in a layer-by-layer fashion. These attributes make ALD an ideal method for applying very precise, conformal coatings over porous materials. In this presentation, we describe recent work exploring the ALD coating of two porous solids: anodic aluminum oxide (AAO) and silica aerogels. The AAO and silica aerogels have been successfully coated by ALD with a variety of oxide films including Al@sub2@O@sub3@, ZnO, TiO@sub2@, Y@sub2@O@sub3@ and V@sub2@O@sub5@ as well as several metals. These materials were characterized with a host of analytical techniques including SEM, TEM, EDX, AFM, XRD and BET surface area measurements. The ALD coated AAO materials are being employed as mesoporous catalytic membranes as well as size-specific separations membranes. To fabricate the catalytic membranes from the AAO templates, the pore diameter of the AAO membranes is first reduced to the 5-10 nm regime using Al@sub2@O@sub3@ ALD. Next, TiO@sub2@ ALD is used to deposit several monolayers of catalytic support material. Finally, the active V@sub2@O@sub5@ catalyst is deposited by ALD. The resulting nanostructured catalytic membranes show remarkable selectivity in the oxidative dehydrogenation of cyclohexane when compared to conventional powder catalysts. Silica aerogels have the lowest density and highest surface area of any solid material. Consequently, these materials serve as an excellent substrate for fabricating catalytic materials by ALD. In addition to their use as catalysts, the ALD modified aerogel materials have applications in hydrogen storage and production, chemical sensing, and optics. In this study, both thin film and monolithic aerogels were coated by ALD and the coating process was investigated as a function of the reactant exposures.

11:20am **TF2-TuM10 High Reflectivity X-Ray Mirrors from W/Al@sub 2@O@sub 3@ Nanolaminates Fabricated by Atomic Layer Deposition***,* ***F.H. Fabreguette****, Z.A. Sechrist, R.A. Wind, S.M. George,* University of Colorado

Nanolaminates can display novel optical, thermal, electrical or mechanical properties. In this study, atomic layer deposition (ALD) was used to fabricate W/Al@sub 2@O@sub 3@ nanolaminates for x-ray mirrors. High x-ray reflectivity depends on precise thickness control, minimal interfacial roughness and high density contrast between the absorber (W) and spacer (Al@sub 2@O@sub 3@) layers in the superlattice that defines the Bragg mirror. The sequential, self-limiting ALD surface reactions allow for atomic control of each layer thickness. Al@sub 2@O@sub 3@ ALD films are amorphous, whereas W ALD films are polycrystalline. To minimize the surface roughness, the W ALD growth temperature was decreased from 177°C to 125°C. This temperature reduction lowered the surface roughness and also changed the tungsten crystalline phase from the @alpha@-phase with some @beta@-phase to the pure @alpha@-phase. This transformation is desirable because the @alpha@-phase has a higher density than the @beta@-phase. Quartz crystal microbalance (QCM) was used as an in-situ probe to optimize the nucleation of Al@sub 2@O@sub 3@ ALD on W and W ALD on Al@sub 2@O@sub 3@ at 125°C. Atomic force microscopy (AFM) studies revealed that smoother films resulted from nanolaminates that had shorter nucleation periods. The optimized W/Al@sub 2@O@sub 3@ nanolaminate growth parameters were used to grow W/Al@sub 2@O@sub 3@ x-ray mirrors. These Bragg mirrors were fabricated with variable bilayer thickness, D, spacer-to-absorber ratio, @gamma@, and number of bilayers, N. The measured x-ray reflectivities were compared with the predicted x-ray reflectivities from the Fresnel equations. Reflectivities as high as 70-80% were obtained using the best set of D, @gamma@ and N parameters. These results demonstrate that the W/Al@sub 2@O@sub 3@ nanolaminates fabricated by ALD are competitive with commercial x-ray mirrors prepared using sputtering techniques.

11:40am **TF2-TuM11 Atomic Layer Deposition of Nickel Oxide Films Using Ni(dmamp)@sub 2@ and Water***, T.S. Yang, W. Cho, M. Kim, K.-S. An, T.-M. Chung, C.G. Kim,* Korea Research Institute of Chemical Technology*;* ***Y. Kim,*** Korea Research Institute of Chemical Technology, South Korea

A novel precursor synthesized for the chemical vapor deposition of metallic nickel, Ni(dmamp)@sub 2@ (dmamp = 1-dimethylamino-2-methyl-2-propanolate), has been tested for its use as a nickel source for the atomic layer deposition of nickel oxide (NiO) using water (H@sub 2@O) as the oxygen source. The precursor is a solid at room temperature, but readily sublimes at 90 °C. The ALD temperature window for this precursor is between 90 °C and 150 °C. The NiO films deposited on Si(001) at 120 °C were characterized by x-ray diffraction, x-ray photoelectron spectroscopy, scanning electron microscopy, and atomic force microscopy. The growth rate of the films was found to be ~0.8 Å/cycle by ellipsometry. The XRD pattern showed no distinct peaks for NiO, indicating that the films deposited at this temperature were amorphous. XPS analysis showed the films to be stoichiometric with some carbon impurities. For a film with the thickness of 820 Å (with 1000 cycles) the rms surface roughness was only ~4 Å as measured by AFM. To elucidate the ALD mechanism of the Ni precursor with water, a quadrupole mass analyzer was employed using D@sub 2@O in lieu of H@sub 2@O. It was found that after a Ni precursor pulse no reaction seemed to take place, however, after a D@sub 2@O pulse, decomposition of the precursor was detected. It is speculated that when the precursor is sent to the substrate (or growing film) it is coordinated to the surface OH groups and when water is introduced, it undergoes a decomposition process to produce a hydroxylated nickel oxide surface. At present, an effort is being made to reduce the amount of carbon impurities. We are also trying to devise a method to deposit metallic nickel using this precursor.

Tuesday Lunch, November 16, 2004

Exhibitor Workshop
Room Exhibit Hall B - Session EW-TuL

Innovations in Vacuum Techniques and Measurements

Moderator: S. Goldfarb, Exxustech

12:20pm **EW-TuL2 Residual Gas and Improved Pressure Control Resolution using a Cryocooled Water-Pumping Throttle Valve***, **H. Grover**,* MeiVac Inc.*; N. GurArye,* Ricor

Precise pressure and residual gas control are critical to quality, yield and profitability. Contamination control and process response/recovery advantages of Downstream versus Upstream pressure control will be discussed using multiple feedback and throttling schemes. Valve geometry and actuation methods determine maximum and minimum conductance, as well as, linearity and resolution of the throttling curve. Concepts of linear throttling control and differential pumping of residual gas will be offered including test data correlated with theoretical calculations. Throttling normally restricts flow of all gaseous components. Experimental data will be presented offering differential pumping of condensables (primarily water vapor) while throttling process gases with a high differential pumping ratio. Advantages and disadvantage of Meissner, flow through cryo water vapor pumps and appendage cryo water vapor pumps will be technically and economically compared to a combined package cryocooled water pumping throttle valve. Species range specific condensable pumping control will be presented using a unique externally controlled servo motor driven cold head instead of the conventional pneumatic driven cryo mechanism. Practical examples will be displayed using advanced cryo technology that allows self-contained cryo cooled throttle valves with no cryo compressor required.

1:00pm **EW-TuL4 A Shuttle System for Rapidly Transfering Components Into and Out of a Vacuum Chamber***, **R.E. Trillwood**,* Electron Beam Engineering Inc.

Shuttle System for transferring parts into and out of a high vacuum system. The Shuttle System was invented in 1988 to enable the rapid production of parts with an electron beam welding machine. Traditionally multiple fixtures are used to load several parts into the vacuum chamber; this amortizes the evacuation time over the number of parts. However the disadvantages are that it is a "batch" operation and it does not eliminate the evacuation time from the process. The Shuttle consists of a piston and cylinder normally mounted on the side of the vacuum work chamber and fitted with a pre-pumping stage. The part, or parts for processing are loaded into a breech cut into the piston and transferred into the chamber, stopping momentarily at the pre-pumping stage. The uniqueness of the system is in the displacement of the seals in the piston and cylinder, which facilitates transfer of parts without a pressure rise in the work chamber. Since the Shuttle volume is usually small compared to the work chamber volume there is the added advantage of "volume sharing" to dilute any residual pressure in the breech as it is transferred. For example the pre pumping stage is typically at a pressure of 100 mili torr but with "volume sharing" as the breech enters the larger work chamber there is no noticeable pressure rise. If a higher level of vacuum is required then it is only necessary to provide a higher level in the pre pumping stage. Today there are several Shuttles in operation, which have produced in excess of a million welded parts with production rates of over 250 parts per hour. It is anticipated that there are many more vacuum applications in industry that could use this invention. Richard Trillwood Patents "Shuttle system for rapidly manipulating a work piece into and out of an atmospherically controlled chamber for doing work thereon in the chamber" Patent number 5,062,758 and4,968,206. Trillwood 4/27/2004.

1:20pm **EW-TuL5 Triple Gauge, A New Combination Vacuum Gauge***, **M. Wuest**, R. Enderes, U. Waelchli,* INFICON Ltd, Liechtenstein

We have developed a new type of combination vacuum total pressure gauge. The gauge combines a Bayard-Alpert, a Pirani and, as a novelty, a capacitive diaphragm gauge (CDG) in one housing of less than 30 mm diameter and 60 mm in length. Up to now this was the size of the most modern Pirani Bayard-Alpert gauges. The gauge has a large measurement range from 5*E-10 mbar to 1500 mbar. Compared to the previous Bayard-Alpert Pirani combination gauge, the addition of a CDG provides gas type independent pressure measurement above 10 mbar. This solves venting problems with different gas types such as argon or helium and is therefore ideal for load lock applications. The integrated Pirani sensor protects the yttrium oxide coated iridium filament of the Bayard-Alpert gauge from premature burnout and bridges the pressure range between the Bayard-Alpert (5*E-10 mbar to 1*E-2 mbar) and the CDG measurement range (10-1500 mbar). This new combination is realized thanks to a novel miniature ceramic CDG. The 11 mm diameter alumina CDG has a reference vacuum in the 1*E-4 mbar range. The pressure is sensed by measuring the deflection of an 80 micrometer thick diaphragm over a gap distance of 15 micrometer. The resolution is 0.2% of measured value over a range of 100-1500 mbar. In addition, one version of the gauge includes an absolute atmospheric pressure sensor for even more accurate load-lock application. A combination gauge saves cost for the original equipment manufacturer as it reduces system requirements such as the number of flanges and cables required as well as software interfaces and testing time. We will give an overview of the sensing principles and sensors involved and present pertinent specifications of the gauge.

1:40pm **EW-TuL6 Impact of Chamber Matching and Process Capability Through Flow Measurement and Adjustment***, **S.A. Tison**, D. Leet, C. Adcock, S. Lu,* Mykrolis Corporation

To ensure process transparency when replacing mass flow controllers (MFC) or when employing new types of mass flow controllers in a particular process, it is often desired to have the flow rate of the replacement MFC match the flow rate of the previously installed MFCs. This can be accomplished in one of two ways. The first way is the most traditional and relies on the inherent accuracy of the MFCs, calibrated traceable to national standards. The second method relies upon an alternate standard, often the tool flow verification methodology. To accomplish the second method requires that the replacement MFC must effectively be recalibrated â?oon-toolâ?⍰ to match the output of the previous MFC. The most common method to achieve this is to use the process tool as the flow measurement standard and obtain flow data on the MFC prior to removal. After the replacement MFC is installed the same data is taken and the new MFC is adjusted to achieve the same output as previously determined with the original MFC. In addition to process transparency, the replacement or a new MFC may be adjusted on tool to ensure that the flow measurements of the MFC agrees with the process tool flow measurements to within a specified tolerance. Inherent to the technique of adjusting the MFC on the tool is the belief that the flow measurement as established by the tool is the best metric to improve process repeatability and reproducibility. This paper will not attempt to validate this claim, but focuses on how these two techniques are implemented with digital mass flow controllers and process implications.

Biomaterial Interfaces
Room 210D - Session BI-TuA

Biomembranes on a Chip

Moderator: J.Y. Wong, Boston University

1:40pm **BI-TuA2 Binding and Aggregation of @alpha@-Synuclein on Supported Lipid Bilayers***, **J.S. Hovis**, E.A. Gamble, M.C. Hull, J.-C. Rochet,* Purdue University

Interest in @alpha@-synuclein was initiated with the observation that two mutations in the @alpha@-synuclein gene are linked to an early onset form of Parkinson's disease. @alpha@-Synuclein was further implicated in Parkinson's disease when the protein was found to be the main component of Lewy body inclusions in the brains of Parkinson's disease patients. In solution @alpha@-synuclein is natively unstructured while in the Lewy bodies it is primarily @beta@-sheet in character. It has been shown that @alpha@-synuclein readily binds lipid vesicles containing negatively charged lipids and that upon binding the protein adopts an @alpha@-helical conformation. Interestingly, the aggregation of @alpha@-synuclein into @beta@-sheet fibrils appears to be enhanced in the presence of negatively charged lipids. Due to the small size of the vesicles used in the previous studies the growth of the aggregates could not be observed directly. To provide more insight into the necessary conditions for the aggregation of @alpha@-synuclein we have observed the binding of @alpha@-synuclein to supported lipid bilayers using epi-fluorescence microscopy and infrared spectroscopy. The extent of aggregation was observed to depend on time, salt concentration, protein concentration and lipid composition. Results will be presented highlighting the necessary conditions for aggregation and comparing the conditions needed for wild-type aggregation with those of two mutant proteins (A30P and A53T) which have been linked with early onset Parkinson's.

2:00pm **BI-TuA3 Bioanalytics in the Nanometer and Attoliter Range***, **H. Vogel**,* Swiss Federal Institute of Technology Lausanne, Switzerland **INVITED**

Spatial compartmentalisation is a prerequisite for the creation of living matter. Without the existence of clearly defined borders, differentiation and diversity at the cellular level would not be possible. Most scientific disciplines that deal with dissolved molecules are concerned with the same problem of subdividing solutions in miniaturised autonomous units, either to increase the functional complexity of a system, reduce reagent consumption, monitor fast chemical kinetics or even to study single-molecules. I will report on our recent progress that allows the massively parallel isolation of attoliter- sized artificial and native, cell-derived vesicles and their self-assembled positioning with 100-nm precision in ordered arrays on surfaces. The broad application for investigating (bio)chemical reactions and cellular signaling processes in individual containers by electrical and optical techniques will be discussed. The biological processes which will be presented are mediated on and across cellular membranes via transmembrane receptors such as transport-, channel-proteins or G protein-coupled receptors to mention some important examples. Our novel approaches are important for the elucidation of the molecular basis of receptor function and signal transduction processes as well as for applications in the field of screening for novel therapeutic compounds.

2:40pm **BI-TuA5 Construction and Characterization of Planar Lipid Bilayers Supported on Conductive Thin Polymer Films: Toward Artificial Photosynthetic Supramolecular Devices***, **L. Wang**, T. McBee, S. Marikkar, C. Ge, N. Armstrong, S. Saavedra,* The University of Arizona

We are developing a new type of biomimetic photosynthetic device based on a photoactive lipid bilayer supported on a planar optical waveguide electrode overcoated with indium-tin oxide (ITO). The bilayer serves as a host for incorporation of artificial photosynthetic centers, which are prepared by Moore, Gust, and Moore (Arizona State University). A water-swollen, conductive polymer cushion is used to couple the bilayer to the ITO surface. The polymer cushion is required to planarize the ITO support and render it compatible with vesicle fusion, as well as act as a transducer of light-generated proton flux across the lipid layer, so that changes in flux can be detected both electrochemically and spectroscopically. In this presentation, we will summarize recent progress in preparation and characterization of lipid bilayers deposited on conductive polymer films composed of poly(aniline) (PANI) and poly(acrylic acid) (PAA), which are deposited by layer-by-layer self-assembly on ITO. A variety of lipid compositions, polymer compositions, and assembly conditions have been compared. An array of methods has been used to characterize these assemblies, emphasizing the diffusive properties of the lipid components, the spectroscopic and electrochemical responses of the PANI/PAA film, and the barrier properties of the lipid layer. Different lipid systems exhibit different diffusive properties; these appear to be correlated with the degree to which the potentiometric response of the PANI/PAA is blocked by lipid bilayer deposition. Egg phosphatidylcholine/cholesterol appears to form a continuous, nearly pinhole free bilayer on 2(PAA/PANI)/ITO, which is attributed to the role of cholesterol as a stabilizer in supported lipid films.

3:20pm **BI-TuA7 Nanoscale Dissection of a T Cell Immunological Synapse***, **J.T. Groves**,* University of California, Berkeley **INVITED**

Coordinated rearrangement of cell membrane receptors into large-scale patterns is emerging as a broadly significant theme of intercellular signal transduction. In an effort to help unravel the mechanisms governing protein organization at intercellular synapses and the role of this organization in signal transduction, we have dissected living T cell immunolgical synapses in a hybrid live cell - supported membrane configuration. Nanometer-scale patterns of fluid lipid membranes, displaying cell recognition and signaling molecules, have been constructed on solid substrates by a combination electron-beam and scanning-probe lithographic techniques, along with membrane self assembly. When doped with appropriate proteins, supported membranes mimic and antigen presenting cell and can form synapses with living T cells. The substrate nanostructures guide the mobility of membrane-linked proteins and, correspondingly, the motion of their cognate partner proteins within living cells. A critical feature of this strategy is that proteins displayed in the supported membrane exhibit diffusive mobility. This enables formation of functional synaptic structures with living cells by permitting the necessary protein rearrangements. The manner in which precisely defined geometrical restrictions frustrate or facilitate synapse formation and signaling in living cells can be used to elucidate the mechanisms and functional consequences of molecular patterns at intercellular synapses.

Electronic Materials and Processing
Room 304B - Session EM-TuA

Defects and Interfaces in Electronic Materials and Devices

Moderator: L.J. Brillson, The Ohio State University

1:20pm **EM-TuA1 Spectroscopic & Microscopic Characterization of Multi-layered Superconducting Thin Films***, S.M. Mukhopadhyay, S. Krishnaswami, **S. Vemulakonda**,* Wright State University

Correlation of chemical composition profile, microstructure & electrical properties of thin film superconductors will be presented in this talk. Studies have been performed to compare the chemical and compositional profiles, grain texture and critical current densities of Y-Ba-Cu-Oxide layers grown by PLD and MOCVD on single crystals and on polycrystalline metal substrates and different buffer (diffusion barrier) layers. X-ray Photoelectron Spectroscopy (XPS) has been used in conjunction with ion beam sputtering to obtain composition and chemistry information at different depths into the film. It is seen that variations in overall composition such as cationic ratios and diffusion of buffer layer species can occur in some types of film. MOCVD samples grown on IBAD textured buffer layers have higher copper concentration that may be linked to higher grain boundary content. Some films grown on polycrystalline metal-substrates (buffered with YSZ and CeO2) show Zr diffusion into the YBCO region whereas those grown on single crystal YSZ (buffered with CeO2) do not. The durability and stability of these films, and their dependence on starting microstructures has been compared and will be presented.

1:40pm **EM-TuA2 Characterization of Hydrogen Complex Formation in InP:Zn (100)***, **M.D. Williams**, S.A. Yasharahla, S.C. Williams, N. Jallow,* Clark Atlanta University

Ultraviolet photoemission spectroscopy is used to study the kinetics of the H-Zn complex formation in Zn doped InP (100). Hydrogen injected into the material electronically passivates the local carrier concentration.@footnote 1@ Reverse-biased anneals of the InP show a dramatic change in the work function of the material with increasing temperature. Spectral features are also shown to be sensitive to sample temperature. To our knowledge, we show the first view of hydrogen retrapping at the surface using photoemission. A simpe work function analysis shows the state of passivation of the material. @FootnoteText@ @footnote 1@ W. C. Dautremont-Smith, Mat. Res. Soc. Symp. Proc. 104, 313 (1988).

2:00pm **EM-TuA3 In situ Studies of Stacking Fault Formation in Silicon Carbide**, ***A. Galeckas,*** *J. Linnros,* Royal Institute of Technology, Sweden; *P. Pirouz,* Case Western Reserve University **INVITED**

Silicon carbide (SiC) has long been recognized as one of the leading semiconductors for high-power applications. Recently, commercial implementation of 4H-SiC material in high-voltage bipolar electronics has seriously been obstructed by a phenomenon causing degradation of electrical characteristics. In this paper we will address the internal causes of degradation by presenting an overview of in situ studies of structural instabilities within active area of SiC device. Several applications of a novel time-resolved pump-probe imaging spectroscopy technique, recently developed by our group for studies of stacking fault (SF) nucleation and expansion dynamics, will be presented in conjunction with conventional TEM measurement results. More specifically, in our method an intense optical excitation is employed to provide excess carriers and to trigger recombination-enhanced motion of dislocations (REDM), whereas dynamics of defects is monitored by time-lapse imaging of the background luminescence, set by a low-intensity probe cw-excitation. We report optically induced nucleation, multiplication and rapid expansion of SF defects and provide experimental evidence of their detrimental impact on carrier transport properties. Our results show that degradation phenomenon is not restricted to the device's active area – stacking faults likewise nucleate and expand on the outside as well as in the standalone epilayers. This fact essentially discards common assumptions that heavy doping of P+ layer and residual mechanical stress at P+/N junction are almost certain SF nucleation sources. In contrast, statistical analysis of PL imaging results strongly suggests that the pre-existing growth defects, for the most part threading screw dislocations, are the major nucleation sources of SFs. Temperature and excitation dependencies of optically stimulated dislocation glide have been quantified, providing an activation enthalpy of 0.25±0.05 eV, which is consistent with energy estimated from the electrical REDM experiments. We discuss the observed differences of glide velocities in terms of possibly different origin of dislocation partials (silicon-core versus carbon-core) and propose the anti-phase defects (APD) on the dislocation partials as likely sites for the kink-pair nucleation. Finally, in view of the important experimental observation that similar formations of SFs could be optically-induced also in p-type material and in 6H polytype, we conclude that degradation phenomenon seems to be rather a general problem of hexagonal SiC material than that of a bipolar device.

2:40pm **EM-TuA5 Spectroscopic Investigation of Epitaxial Dielectrics on SiC**, ***J. Choi,*** *C.M. Tanner, R. Puthenkovilakam, J.P. Chang,* University of California, Los Angeles

SiC has attracted much attention as a promising wide-bandgap semiconductor material due to its excellent physical and electrical properties. Among other SiC- based devices, group-III nitrides on SiC have demonstrated great device performance as blue light-emitting diodes and high electron mobility transistors. In these devises, inclusion of an AlN buffer layer improves the performance due to its good lattice match with SiC substrate and relatively low misfit with the III-nitride layers. In this work, we demonstrate the deposition of HfO@sub 2@, a well known high-k gate dielectric material for silicon based devices, by an atomic layer deposition process on AlN/SiC. During the thin-film growth, the crystallinity of the epitaxial layers is monitored by in-situ reflection high-energy electron diffraction (RHEED) and the thin film composition is characterized by in-situ x-ray photoelectron spectroscopy (XPS). To examine the characteristic electrical properties, capacitance-voltage and current-voltage measurements are performed on HfO@sub 2@/AlN/SiC and HfO@sub 2@/SiC capacitors fabricated by photolithographic patterning of metal electrodes. The correlation between growth conditions, stoichiometry and crystallinity of the eptaxial layer, and device performance will be discussed. Finally, we present first-principle calculations of the valence band structures of AlN and SiC as well as band alignment at the interface, in comparison with the experimentally determined band alignment by XPS. The experimental band offset is determined by measuring the core-level to valence-band maximum binding energy difference for AlN and SiC at an interface, subsequently scaling them with respect to core-level separation between bulk Si and Al, and agrees well with the theoretical prediction.

3:00pm **EM-TuA6 Variation of WNx Gate Work Function after High Temperature Annealing**, ***P.-C. Jiang,*** *J.S. Chen,* National Cheng Kung University, Taiwan

The selection of the gate electrode material has become a critical issue as the dimension of CMOS devices continues to scale down. According to the 2001 ITRS roadmap, WNx is a promising material as the gate electrode for the PMOS transistor, because the WNx has a Fermi level near the silicon valence band. In this work, we investigate the variation of metal work function (Î¦m) of reactive sputtered WNx films after annealing at different temperatures (400-600â"f). The annealing atmosphere is forming gas (N2:H2=135:15) and the annealing time is 30min. By measuring the C-V curves of the MOS structure with oxides of different thickness, we can derive the Î¦m of the WNx gate. After annealing, the phases of the WNx films had changed and their nitrogen contents also varied due to the out-diffusion of nitrogen to the ambient. The variation of nitrogen content in WNx upon annealing will lead to the change of Î¦m. By measuring the I-V curves of the MOS structure with reverse bias, the leakage current increases with decreasing the Î¦m. As a result, the Î¦m not only affects the threshold voltage of the device but also changes the leakage current of the oxide layer, and the nitrogen content in WNx is the key point to determine the Î¦m.

3:20pm **EM-TuA7 New Mechanisms for Controlling Transistor Junction Formation through Surface Chemistry**, *E.G. Seebauer,* ***K. Dev,*** *C.T.Z. Kwok, R.D. Bratz,* 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 two distinct ways to employ adsorption at the surface for this task: adjusting the intrinsic loss rate of interstitials to the surface, and reducing the degree of electrical charge built up at the surface. We control the interstitial loss rate to the surface by saturating dangling bonds using adsorbed nitrogen, introduced as ammonia, hydrazine, or a similar simple gas 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. The annealed profiles with adsorbed N change more, and the profiles with a rather thick layer of adsorbed O has change the most. Electrical charge that builds up at dangling bonds on a surface couples to charged defects in the underlying bulk through an electric field near the surface that strongly repels the bulk defects. The strong repulsion in the near-surface region in effect makes the surface more reflecting of interstitials, thereby changing the concentration profile of the bulk defects and correspondingly in the dopant profile. We have shown by the optical method of photoreflectance that nitrogen adsorption greatly reduces the charge buildup at the surface, and therefore reduces the surface repulsion effect.

3:40pm **EM-TuA8 Annealing Effect on Dielectric Properties of Ti Doped K(Ta,Nb)O@sub 3@ Thin Film using PLD**, ***H.-J. Bae,*** *J. Sigman,* University of Florida; *L.A. Boatner,* Oak Ridge National Laboratory; *D.P. Norton,* University of Florida

K(Ta,Nb)O@sub 3@ (KTN) has been widely studied for optical wave guides and tunable microwave applications. In this study, the reduction of dielectric loss by acceptor ion doping is investigated for epitaxial thin films. Acceptor doping traps electrons due to oxygen vacancies that form during oxide film growth. Epitaxial KTa@sub 0.524@Nb@sub 0.446@Ti@sub 0.03@O@sub 3@ films with 3% Ti were investigated. The KTN:Ti films were grown at 750@super o@C using pulsed laser deposition. The dielectric properties of Ti doped KTN films were measured for unannealed and annealed films. Annealing temperatures ranged from 800@super o@C and 1000@super o@C in an oxygen ambient. The dielectric properties of KTN:Ti films obtained after annealing are compared with that for as-deposited KTN:Ti film and undoped KTN films. The crystallinity, surface morphology, and electrical properties were investigated using x-ray diffraction, atomic force microscopy, and dielectric response. This latter involved capacitance measurements of as-deposited and annealed films, measured at 1MHz using interdigitated electrodes. Tunability and dielectric loss of as-deposited KTN:Ti film were determined to be 10% and 0.0134, respectively. For films annealed at 800@super o@C and 900@super o@C, the dielectric loss decreased but with a decrease in tunability as well.

Magnetic Interfaces and Nanostructures
Room 304A - Session MI-TuA

BioMagnetism

Moderator: D.P. Pappas, National Institute of Standards and Technology

1:20pm **MI-TuA1 Synthesis and Surface Modification of Monodisperse Magnetic Nanoparticles for Biological Applications***, **S. Sun**, H. Zeng, H. Yu, D. Robinson,* IBM T.J. Watson Research Center*; G. Li, S. Wang, R. White,* Stanford University **INVITED**

We present our chemical synthesis and surface modification of monodisperse magnetic nanoparticles for potential applications in bio-recognition. Biocompatible dispersions of magnetic nanoparticles have been used widely in bimolecular labeling and biological imaging, sensing and separation in recent years. These applications require that the particles be superparamagnetic at room temperature, and monodisperse for uniform biodistribution, bioelimination and contrast effects. The Co and Fe based magnetic nanoparticles, including metallic Co, Fe, CoFe and oxide MFe2O4 nanoparticles, have high magnetic moment, and thus sufficient sensitivity for magnetic detection. With proper functionalization, they can be useful candidates as magnetic probes for biomolecule identification. We have developed various synthetic procedures for making monodisperse magnetic nanoparticles. Using a combination of surfactants, such as oleic acid/oleyl amine, to control nanoparticle growth and stabilization, we can tune the size of the nanoparticles to obtain an optimum magnetic signal for sensor detection. By controlling particle surface chemistry and synthetic conditions, we can also produce multi-functional nanoparticles with either core/shell-structured particles, such as Fe3O4/AgSe or Fe3O4/FePt, or dumbbell-structured particles, such as Fe3O4-Ag. We can further transform the oleic acid/oleylamine capped, hydrophobic nanoparticles into hydrophilic ones by using tetramethylammonium hydroxide, bi-functional thiol molecules, or multi-functional polymeric molecules. These hydrophilic nanoparticles are both chemically and magnetically stable in phosphate buffer solution at neutral pH, and can withstand DNA denaturing and hybridization conditions. They are suitable as magnetic probes for highly sensitive bio-detection. Acknowledgement: The work is supported in part by DARPA under grant No. N00014-01-1-0885.

2:00pm **MI-TuA3 Progress in Non-Invasive Biomagnetic Liver Iron Store Measurements***, **D.N. Paulson**,* Tristan Technologies **INVITED**

Biomagnetic liver susceptometry is a non-invasive measurement of liver (and spleen) iron stores. Proposed by Bauman in 1967, it was demonstrated on animals@footnote 1@ shortly thereafter. With the development of the Superconducting quantum interference device (SQUID) magnetic field sensor, a prototype system was developed for measurement of human liver iron stores. Measurements on normal and iron overloaded subjects showed this technique to be an accurate quantitative measurement of human iron stores@footnote 2@. The basic system is comprised of a superconducting magnet, a highly sensitive SQUID magnetic field sensor, a water bag (placed between the sensor and patient) that simulates the natural magnetism of the body, a non-magnetic bed and data acquisition system. Since the installation of the first clinical systems at Cleveland and Hamburg, over 6,000 clinical measurements have been made on over 4,000 patients. We describe the measurement technique and present summaries of a number of clinical studies comparing biomagnetic liver susceptometry to needle biopsies. We describe the current status of both the original systems@footnote 3@ and improved systems now being produced and comment on future directions in the non-invasive measurement of liver-iron stores including the possibility of assessment of cardiac iron. @FootnoteText@ @footnote 1@ Bauman JH, Harris JW, "Estimation of hepatic iron stores by in-vivo measurement of magnetic susceptibility", J Lab Clin Med 1967; 70: 246-257.@footnote 2@ Brittenham GM, Farrell DE, Harris JW, Feldman ES, Danish EH, Muir WA, Tripp JH, Bellon EM."Magnetic-susceptibility measurement of human iron stores", N Engl J Med 1982; 307: 1671-1675.@footnote 3@ Paulson DN, Fagaly RL, Toussaint RM, Fischer R, "Biomagnetic Susceptometer with SQUID Instrumentation", IEEE Transactions on Magnetics, vol 27, no. 2, March 1991.

2:40pm **MI-TuA5 Design Considerations for High Sensitivity Biosensing with Magnetic Labeling and Detection***, **J.C. Rife**,* Naval Research Laboratory **INVITED**

We are developing the BARC (Bead ARray Counter) sensor chip for the detection of biomolecules labeled with magnetic microbeads.@footnote 1@ Presently, 2.8 µm-diameter commercial magnetic beads are detected by an array of 64 GMR sensors on the chip, with each sensor spanning a 200 µm diameter spot. Arrays of single-stranded DNA or antibody probes are immobilized onto the sensor spots, and biomolecular targets (e.g. DNA or proteins) that are captured by the probes are then labeled with magnetic microbeads. Although at the limits of detection each bead labels a single captured molecule, non-specifically bound beads and sensor noise currently set the limit of detection to about 10 beads (potentially 10 molecules) per sensor. Although the sensor signal to noise can be improved, ultimately the sensitivity will be limited by delivery of molecules to the sensor surface as governed by diffusion, sensor geometry, and fluidics. The current BARC sensor array has an advantage because of its relatively large sensors, and can presently detect DNA concentrations as low as 1 fM (10@super 5@ molecules/cm@super 3@). Further improvement in the sensitivity will require coupling the design of the fluidics with the sensor array. I will discuss the BARC sensor response, along with finite element calculations of the delivery of molecules to the surface under various conditions. I will also discuss how these issues affect various alternative magnetic labeling and detection approaches, such as those based on spin valves and SQUIDs. This work done in collaboration with M. M. Miller, P. E. Sheehan, C. R. Tamanaha, M. Tondra, and L. J. Whitman. @FootnoteText@ @footnote 1@J. C. Rife et al., Sensors and Actuators A 107, 209-218 (2003).

3:20pm **MI-TuA7 Advances in MR Elastic Displacement Imaging and Non-invasive Measurements of Myocardial Compliance***, **H. Wen**,* NHLBI/NIH **INVITED**

The vector nature of the NMR signal gives rise to a group of displacement imaging methods in magnetic resonance imaging that are based on spin phase-shifts. They are suited for studying physiological motions such as the heartbeat and elastic reponses of arterial walls to the blood pressure. Elevated myocardial stiffness is a cause of high diastolic blood pressure and congestive heart failure. The traditional measure of heart chamber stiffness uses diagnostic catheterization, an invasive procedure not acceptable for many patients. MR elastic displacement imaging is a new way to estimate material viscoelastic parameters non-invasively. It has been validated in animal models and shown feasible in humans. Clinical trials to detect heart and artery stiffening in patients with congenital heart disease are being prepared.

MEMS and NEMS
Room 213C - Session MN+MS+PS+TF-TuA

Nano/MEMS Manufacturing and Plasmas

Moderator: R. Ghodssi, University of Maryland

1:20pm **MN+MS+PS+TF-TuA1 Wafer-Level, Low-Cost, High-Vacuum Packaging of MEMS Devices Using Nanogetter TM***, **N. Najafi**, D.S. Sparks,* Integrated Sensing Systems, Inc. (ISSYS) **INVITED**

As part of its development effort to commercialize a Micro-Density Meter, ISSYS Inc. invented a new technology for long-term, low-cost, wafer-level, high-vacuum, hermetic encapsulation of MEMS devices. This technology is now commercially available through a spin-off company: Nanogetter Inc. At the system level perspective, one of the most attractive features that NanogetterTM offers to the MEMS community is a "Total Solution" to an important problem facing many emerging MEMS products. Nanogetters Inc. technology offers: Wafer-level, high-vacuum (< 1mTorr) encapsulation, Long-term vacuum stability, Hermetic electrical lead transfer, Compatibility with all MEMS technologies (polysilicon surface, bulk, silicon-on glass, and LIGA micromachining technologies), High yield, Low cost In addition to high-vacuum packaging applications, NanogetterTM will be further developed to provide ambient environments suitable for applications requiring higher pressures. For example, for micro-switches and accelerometers, the technology will absorb humidity and oxygen. As a testbed for using this wafer-level, high-vacuum technology, the performance of a micro-density meter will be presented.

2:00pm **MN+MS+PS+TF-TuA3 Low-Pressure and Plasma-Enhanced Chemical Vapor Deposition Modeling at the Feature Length Scale of MEMS Devices***, **L.C. Musson**,* Sandia National Laboratories*; P. Ho,* Reaction Design*; R.C. Schmidt,* Sandia National Laboratories

Theoretical modeling of the surface chemistry and concomitant surface evolution during MEMS fabrication processes has great potential for improving surface micromachining (SMM) process technologies. A greater understanding of the fundamental factors leading to surface non-uniformities and other non-ideal geometric artifacts can lead to better device designs and assist in process optimization. We are developing

ChISELS, a parallel code to model material deposition and etch processes at the feature scale. ChISELS uses the level-set method which was chosen for its natural ability to handle substantial changes in topology that occur when fabricating MEMS devices. We describe the algorithm by which the surface is evolved in process models, the transport model, the tools used for modeling chemical reactions and dynamic balancing of the computational load in a parallel environment. The capabilities of the ChISELS code are demonstrated by models of low-pressure deposition of SiO2 from TEOS and from a silane/oxygen/argon plasma. The uniformity of deposition into various geometries has been studied and will be presented in both 2-D and 3-D models. Some comparisons between the predicted deposition geometries and experimental SEMs will also be shown.

2:20pm **MN+MS+PS+TF-TuA4 Detection of Metal Film Deposit Smoothness by a MEMS-NEMS Structure via Surface Plasmon Effects***, **D.T. Wei**,* Wei & Assoc.*; A. Scherer,* California Institute of Technology

A thin metal film under strong illumination, from uv to visible, will induce a quantum effect of electron plasma called surface plasmon effect. When the film is a deposit on a semiconductor surface, it takes additional structure in submicron scale to make an electronic detector. This detection method has high potential for controlling the smoothness of metal coating by traditional plasma or by ion beam deposition. Such an integrated structure is effective to detect the surface roughnesses vs. plasmon modes not often obtainable through other means, such as their decay products. A NEMS device is designed and fabricated for collecting electrons from the decaying surface plasmons in avalanche mode. The signal responds to the degree of the metal deposit surface roughness down to nano, even subnano sizes. Imperfections in metal film resulted from thermal plasma deposition are theoretically analyzed and relevant data are presented from the nano structure with new insights. Assembled unit will be applicable to monitoring the metal coating smoothness. Applications in transparent electroding and adaptive optics are sought.

2:40pm **MN+MS+PS+TF-TuA5 Etching of High Aspect Ratio Structures in Si using SF@sub 6@-O@sub 2@-HBr and SF@sub 6@-O@sub 2@-Cl@sub 2@ Plasmas***, **S. Gomez**, J. Belen,* University of California, Santa Barbara*; M. Kiehlbauch,* Lam Research Corporation*; E.S. Aydil,* University of California, Santa Barbara

Plasma etching of high aspect ratio (depth-to-width) structures in Si is a crucial step in manufacturing trench capacitors for memory devices, and integrated components for microelectromechanical systems (MEMS). We have investigated etching of deep (~3-10 µm) and narrow (~0.2-0.5µm) features with high aspect ratios (~10-50) using plasmas maintained in mixtures of SF@sub 6@, O@sub 2@ and HBr gases, and in mixtures of SF@sub 6@, O@sub 2@ and Cl@sub 2@ gases as an alternative to the Bosch process. Experiments were conducted in a low pressure (25 mTorr), high density, inductively coupled plasma etching reactor with a planar coil to maintain the discharge and with radio frequency (rf) biasing of the substrate electrode to achieve independent control of the ion flux and ion energies. Specifically, we have studied HBr and Cl@sub 2@ addition to SF@sub 6@/O@sub 2@ plasmas and O@sub 2@ addition to SF@sub 6@/HBr and to SF@sub 6@/Cl@sub 2@ plasmas. We have analyzed the effect of these additions on the etch rate and feature profile using Si wafers patterned with 0.2 µm diameter holes in a SiO@sub 2@ mask. Visualization of the profiles using SEM is complemented by plasma diagnostics such as optical emission and mass spectroscopies to understand the key factors that control the anisotropy and etch rate. Upon adding HBr to an SF@sub 6@/O@sub 2@ plasma, a silicon oxybromide film forms on the sidewall, reducing undercut and increasing taper. However, subsequent reduction of O@sub 2@ gas increases mask undercut and isotropic etching by reducing sidewall oxidation. On the other hand, adding Cl@sub 2@ to an SF@sub 6@/O@sub 2@ plasma causes a reduction of O density and a weak silicon oxychloride film forms on the sidewall. This chlorinated film is more easily etched by F, therefore increasing mask undercut. Subsequent reduction of O@sub 2@ gas further increases mask undercut and isotropic etching.

3:00pm **MN+MS+PS+TF-TuA6 Deep Reactive Ion Etching of Silicon Structures for Profile and Morphology Control***, **R.J. Shul**, M.G. Blain, S.G. Rich, S.A. Zmuda,* Sandia National Laboratories

Deep reactive ion etching (DRIE) of Si or the Bosch process relies on an iterative etch/deposition process where a sidewall etch inhibitor is formed to prevent lateral etching of the Si thus resulting in highly anisotropic etch profiles at reasonably high etch rates. The formation of deep, high-aspect ratio, straight-wall Si structures achieved with this process has been used to fabricate chemical and biological sensors, micro-fluidic devices, and mechanical actuators and gears. However as device designs become more complicated and aspect ratios increase, conventional DRIE processes often cannot meet the demands. For example, high-aspect ratio features etched to depths greater than 150 microns often become tapered and rough with unacceptably slow etch rates. This observation is often referred to as RIE lag or aspect ratio dependent etching and is attributed to reduced diffusion of neutral reactants and etch product species and reduced ion transport to the feature bottom as the depth increases. In many cases the etch will actually terminate due to either inefficient etching or polymer deposition dominating the process. We will report on the use of the DRIE platform to fabricate deep, high-aspect ratio Si features incorporating a process in which etch parameters are incrementally varied during each cycle of the process. The use of this in-situ variable etch process has resulted in a high degree of profile control and smooth etch morphologies while maintaining reasonably fast etch rates for high aspect ratio features. Etch results using this process will be reported as a function of cathode power, etch and deposition time, and reactive gas flow. These results will be compared to results obtained using conventional DRIE processes. 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.

3:20pm **MN+MS+PS+TF-TuA7 Fabrication of Wide-IF 200-300 GHz SIS Mixers with Suspended Metal Beam Leads Formed on SOI***, **A.B. Kaul**, B. Bumble, K.A. Lee, H.G. LeDuc,* Jet Propulsion Laboratory, California Institute of Technology*; F. Rice, J. Zmuidzinas,* California Institute of Technology

We report on a novel fabrication process that uses SOI substrates and micromachining techniques to form wide-IF SIS mixer devices that have suspended metal beam leads for RF grounding. The mixers are formed on thin 25 µm membranes of Si, and are designed to operate in the 200 - 300 GHz band. Potential applications are in tropospheric chemistry, where increased sensitivity detectors and wide-IF bandwidth receivers are desired. They will also be useful in astrophysics to monitor absorption lines for CO at 230 GHz, to study distant, highly red-shifted galaxies by reducing scan times. Aside from a description of the fabrication process, electrical measurements of these Nb/Al-AlNx/Nb trilayer devices will also be presented. Since device quality is sensitive to thermal excursions, the new process appears to be compatible with conventional SIS device fabrication technology.

3:40pm **MN+MS+PS+TF-TuA8 Characterization of Polycrystalline AlN Film Quality Using Variable Angle Spectroscopic Ellipsometry***, **L.-P. Wang**, D.S. Shim, Q. Ma, V.R. Rao, E. Ginsburg, A. Talalyevsky,* Intel Corp

Aluminum nitride (AlN) thin films have been investigated for piezoelectric, wide band gap, high-k dielectric and other applications. Recently, AlN films for bulk acoustic wave (BAW) resonators and filters have been studied extensively, driven by the fast growth of wireless communications. For this application, AlN films are mostly prepared by reactive sputtering, a technique with the advantage of low deposition temperature, easy process control and low cost when compared to alternatives such as metal-organic chemical vapor deposition (MOCVD) and molecular beam epitaxy (MBE). Highly c-axis oriented AlN films are desirable for optimal piezoelectric and crystal properties. Currently, X-ray diffraction (XRD) rocking curve is the predominate method for characterizing the crystal and piezoelectric properties. In this study, optical constants of AlN films, refractive index (n) and extinction coefficient (k), were determined by a variable angle spectroscopic ellipsometry (VASE). The microstructure of the sputtered polycrystalline films is well reflected in the VASE optical model, which includes cylindrical symmetry, effective medium approximation (EMA), index gradient, and surface roughness. For the first time, the film optical constants were correlated to the full width at half maximum (FWHM) of XRD rocking curve. It was found that the films with smaller FWHM, an indication of better crystal and piezoelectric properties, had higher n and lower k. This is consistent with the general observation that higher n and k of polycrystalline films typically have fewer defects and better microstructures. The correlation between the optical parameters and the film quality leads to a simpler and faster method for characterizing sputtered AlN films. Furthermore, such optical tools can be integrated in a sputter deposition system for in-situ monitoring of AlN film thickness and quality simultaneously.

Nanometer-scale Science and Technology
Room 213D - Session NS-TuA

Nanostructures and Biology

Moderator: H.G. Craighead, Applied & Engineering Physics

1:20pm **NS-TuA1 Virus & Biomolecule Detection Using Nanoelectromechanical Devices*, B. Ilic,*** *Y. Yang, H.G. Craighead,* Cornell University

We have used resonating mechanical cantilevers to detect binding of viruses and biomolecules captured from liquid. As a model virus, we used a nonpathogenic insect baculovirus to test the ability to immunospecifically bind and detect small numbers of virus particles. Arrays of surface micromachined antibody-coated polycrystalline silicon nanomechanical cantilever beams were used to detect binding from various concentrations of baculoviruses in a buffer solution, by observing the resonant frequency shift of the oscillators. Because of their small mass, the 0.5µm x 6µm cantilevers have mass sensitivities on the order of 10@super -19@ g/Hz, enabling the detection of an immobilized AcV1 antibody monolayer corresponding to a mass of about 3 x 10@super -15@g. With these devices we can detect the mass of a single virus to the cantilever. Resonant frequency shift, resulting from the adsorbed mass of the virus particles, distinguished solutions of virus concentrations varying between 10@super 5@ and 10@super 7@ pfu/ml. Single crystal silicon nanomechanical oscillators with spatially-defined chemical binding sites, with greater mass sensitivity, have similarly been used to detect the binding of specifically bound biomolecules at the attogram level. In both experiments careful controls were done to assure the detected mass resulted from the intended specifically bound biomaterial.

1:40pm **NS-TuA2 Electrokinetic Molecular Separation in Nanoscale Fluidic Channels*, A.L. Garcia,*** The University of New Mexico

We have developed an interferometric lithography technique to manufacture an integrated micro-nano-fluidic chip for use in bioseparations and sensing. Transport behavior of two dyes, one charged and one neutral, in these silica/silica oxide/Pyrex chips has been quantified. A mixture of the dyes was introduced into an array of nanoscale channels using electroosmosis through the microfluidic channels. Electrokinetic separations of the dyes in these nanochannels at various applied biases were examined in different chips with nanochannel widths ranging from 50-200 nm. Confocal laser scanning microscopy was used to observe the average velocities of the dyes in the array of nanochannels. The resulting velocities were in good agreement with theoretical predictions that take into account the wall surface potential overlap and electrolyte concentrations across the individual nanofluidic channels. Separations were also achieved in these channels by the application of pressure, utilizing the Poiseuille velocity distribution of fluid within the channels.

2:00pm **NS-TuA3 Fabrication of Nano-Structured Polymeric Surfaces for Bio-Sensing Devices**, *A. Valsesia,* ***P. Colpo,*** *T. Meziani, M. Manso, D. Gilliland, G. Ceccone, F. Rossi,* EU-JRC-IHCP, Italy

The interaction between material surfaces with specific chemical functionalities and bio-molecules has been widely investigated in order to modulate the performances of bio-sensors and medical devices. When the dimensions of the interacting surface structures are comparable with those of the single protein molecules or small clusters of proteins, the bio-molecules absorption is considerably influenced both from the morphological and chemical point of view. This can be exploited for the orientation of specific binding sites between antigens and antibodies. In this work we develop a reliable technique to produce chemical contrast at sub-micrometric level through the fabrication of nano-island from Poly Acrylic Acid (PAA) film deposited onto anti-fouling substrates. First, a thin layer of PAA is deposited on the substrate by PE-CVD. Then, a layer of polystyrene colloidal nano-particles (200-500 nm) is deposited by spin coating. The nano-particles are then partially removed by oxygen plasma etching of the surface. The etching process is stopped before the complete etching of the nano-particles and the residual ones are removed by ultrasonic bath. Whereas unmasked PAA film is completely etched, nano-domes of as deposited-PAA (located under the nano-mask) are created evenly on the surface. The shape and the 2-D geometry of the resulting PAA nano-domes (lateral distribution, surface density) is controlled by the parameters of the spin casting process and by the wetting characteristic of deposited PAA. The chemistry of the PAA films was characterized by XPS, whilst the resulting nano-structured surfaces have been studied using AFM, SEM, SPM and SIMS in imaging mode. Then protein absorption test have been performed on the nanostrucured surfaces: the SEM and AFM characterization revealed that nanometric proteins clusters are selectively bond on the top of the domes, and not between them where the anti-fouling matrix repels the biomolecules.

2:20pm **NS-TuA4 Hairy Peptide Nanotubes*, M. Biesalski,*** *J. Couet, J.D. Jeyaprakash S. Samuel, S. Santer,* Institute for Microsystem Technology (IMTEK), Germany

A general theme in Nanotechnology is the development of novel materials with well-defined composition and nanometer scale structures. To this, materials scientists are increasingly deriving new lessons from naturally occurring "nanomaterials" about useful composition-structure property relationships that might be mimicked with synthetic materials.@footnote 1@ An interesting example constitutes the bottom-up formation of hollow tubular structures by a spontaneous self-assembly of cyclic peptides. Cyclic peptides consisting of alternating D- and L-amino acids posses a flat conformation that allows the build-up of beta-sheet type assemblies, where the cyclic peptides are stacked onto each other forming a hollow tubular structure with a precisely defined inner diameter and all amino acid residues pointing outwards.@footnote 2@ In order to construct functional polymeric nanotubes we have synthesized cyclic peptides that are modified with an ATRP initiator at distinct side groups ("CP-ini"). The CP-ini self-assembles into nanotubes that present these initiator moieties on the surface. The peptide nanotubes are subsequently coated with different functional polymers by using (living) radical polymerization initiated from the surface of the tubes. The so prepared functional nanotubes are characterized with respect to the dimensions, morphology and higher order assemblies using AFM, TEM and X-ray diffraction. The size of the polymeric shell of the nanotubes can be controlled by adjusting the graft density and the molecular mass of the surface-attached polymer chains. The concept of grafting polymer chains from cyclic peptide assemblies is highly modular with respect to the incorporation of a wide range of different functions. @FootnoteText@ @footnote 1@ M. Tirrell, E. Kokkoli, M. Biesalski, Surface Science 500, 2002, p61-83.@footnote 2@ M.R. Ghadiri, J.R. Granja, R.A. Milligan, D.E. McRee, N. Khazanovich, Nature 366, 1993, p324-327.

2:40pm **NS-TuA5 Atomic Force Microscope Conductivity Measurements of Single Ferritin Molecules*, D. Xu,*** *G.D. Watt, J.N. Harb, R.C. Davis,* Brigham Young University

We will present electrical measurements on the conductivity of ferritin molecules by conductive atomic force microscope (c-AFM). The high structural stability of ferritin molecules, relative to other proteins, makes them attractive for nanotechnology applications such as nanoscale batteries. Ferritin is an iron-storage protein that functions as an iron reservoir in animals, plants, fungi and bacteria. Ferritin consists of 24 protein subunits that are arranged to form a spherical molecule with an external diameter of 12nm. The hollow ferritin interior with a diameter of ~8nm can hold up to 4500 iron atoms as Fe(OH)@sub 3@. For battery applications the electron transfer rate through the ferritins is a critically important parameter; it will affect the internal resistance and limit the maximum current. Ferritin molecules were self-assembled on gold surfaces to form sub-monolayer films and characterized by AFM prior to electrical measurements. Electrical conductivity measurements were performed on both single apoferritin and holoferritin molecules by c-AFM. The conductivity of monolayer films (~ 1 µm@super 2@) of ferritin molecules on atomically flat gold surfaces was measured for comparison. Holoferritin was 5-15 times more conductive than apoferritin, indicating that for holoferritin most electron transfer occurs through the ferrihydrite core. With 1 volt applied, the average electrical current through single holoferritins and single apoferritins was 2.58 pA and 0.188 pA respectively.

3:00pm **NS-TuA6 Friction Measurements of DMPC Phospholipidic Bilayers*, G. Oncins,*** *S. Garcia-Manyes, F. Sanz,* Universitat de Barcelona, Spain

Self-assembled phospholipid layers have been a matter of extensive research during last decades. The high content of these structures in cellular membranes has led to their use as models for the study of a wide bunch of biological, biochemical, biophysical and medical issues. Besides, the Supported Planar Bilayers (SPBs) have been very useful in the study of interaction and adhesion forces between cells, in the modelling of the diffusion kinetics of phospholipids and in the insertion of proteins in membranes. AFM has proved to be the most suitable technique to obtain molecular topographic resolution of these systems and to study the morphology of SPBs under various conditions. We have recently worked with such structures at a nanometric level, mostly performing studies based on AFM force spectroscopy measurements of 1,2-Dimyristoyl-sn-glycero-3-phosphocholine (DMPC) bilayers@footnote 1@. The present work has used Lateral Force Microscopy (LFM) to mechanically test DMPC bilayers supported on mica, performing a series of experiments with laterally and vertically calibrated tips in aqueous environment and in which NaCl concentration has been ramped from 0M to 0.1M. Obtained friction results have been complemented with AFM height images of the same tested bilayer area, being able to relate each friction signal with its corresponding topography. Results have shown that the presence of NaCl modifies drastically the mechanical response of the DMPC bilayer, and, consequently, of the cellular phospholipidic membrane. @FootnoteText@ @footnote 1@Garcia-Manyes, S. ;Oncins, G.; Sanz, F.; Effect of ionic solutions on the nanomechanics of a model lipid bilayer: a quantitative Force Spectroscopy contribution, submitted to JACS Communications.).

Plasma Science and Technology
Room 213A - Session PS+MS-TuA
45nm Node with Panel Discussion

Moderators: B. Ji, Air Products and Chemicals, Inc., G. Oehrlein, University of Maryland

1:20pm **PS+MS-TuA1 Preliminary Investigations for Ultimate Gate Patterning***, E. Pargon,* LTM-CNRS, France*; **J. Foucher,*** CEA-LETI, France*; J. Thiault, O. Joubert,* LTM-CNRS, France

The fabrication of a sub-20nm transistor gate requires a very accurate control and understanding of all the plasma steps (resist trimming, BARC, hard mask open and gate etch) involved in the gate stack processes. Then, it is important to study the parameters that can generate a deviation of the final gate dimension for each of these plasma steps. The two aspects that we have studied are the etching behaviour of the photoresist mask exposed to the plasma, and the chemical nature of the layers that deposit on the reactor walls and feature sidewalls during the process. We have developed an experimental procedure using XPS analyses to characterize the chemical modifications occurring on the tops and sidewalls of the photoresist mask as well as the chemical nature of the coatings formed on the chamber walls. These analyses can be correlated with the process performances (in terms of etch profile and critical dimension control (CD control). SEM observations and CD AFM 3D have been used to get the process performance. In all the plasma conditions investigated, the BARC and hard mask opening steps both lead to a CD deviation of 5 to 15 nm attributed to the modifications of the photoresist mask during plasma exposure. XPS analyses and 3D AFM measurements show that the passivation layers formed on the pattern sidewalls during the gate etch step itself are strongly influenced by the pattern density and etch chemistry. Finally, we show that the only way to control gate etch processes in the sub 20 nm range is to minimize strongly the formation of the passivation layers on the gate sidewalls.

1:40pm **PS+MS-TuA2 EUV Light Source Development and Debris Mitigation For 45nm Node Lithography and Beyond***, **B.E. Jurczyk,** M.A. Jaworski, M.J. Neumann, M.J. Williams, D.N. Ruzic,* University of Illinois at Urbana-Champaign

Discharge-produced plasma (DPP) light sources are leading candidates for generating 13.5-nm wavelengths needed for next-generation optical lithography. Traditional DPP sources have used xenon radiators due to its cleanliness; however, high output requirements (>115W at first focus) are driving developers towards higher conversion efficiency fuels such as tin. As a result, condensable tin vapor and electrode debris reaching and damaging the first collector optic is a serious concern for device lifetime and cost of ownership. A secondary-plasma debris mitigation technique was successfully demonstrated for noble gas light sources at the Illinois Debris-mitigation EUV Applications Laboratory (IDEAL). The IDEAL facility utilizes a dense plasma focus discharge source operating at nominal conditions of 15 J/pulse, 50 Hz rep rate, and 3 kV. Electrode sputtered debris is re-ionized in a secondary plasma region and removed with a biased foil trap prior to the collection optics. For a low density plasma (10@super 9@ cm@super -3@) condition, a debris removal fraction of 61% ± 3% was observed. The experimental chamber has been modified to operate with tin delivery into the pinch region. Results from electrode redesign, tin injection, EUV light output and condensable tin vapor mitigation will be presented. High density results from an improved internal helical-resonator shielded inductive coil configuration give greater protection efficiency. Fast ions contributing to optic erosion have been observed. Results from a gridded energy analyzer shows two peaked ion distributions at 2.8 keV and 5.8 keV. Elevated plasma potential and sheathing effects have shown an increase in ion energy at the boundaries. An improved ESA/TOF system provides < 5 eV spectral energy resolution and information on charge/mass ratio. Preliminary results from the new Surface Cleaning of Optics by Plasma Exposure (SCOPE) facility are presented for advanced fuel interactions on optical components.

2:00pm **PS+MS-TuA3 Fundamental Studies on Low-k Processing***, **T. Tatsumi,*** Sony Corporation, Japan **INVITED**

The need for reliable low-k/Cu interconnect technologies is increasing, and many kinds of low-k materials have been proposed. We need a process design for etching that will correspond to a change in the film densities and compositions of low-k materials for 90 and 65-nm node devices. Using many different in-situ plasma-measuring tools, such as IRLAS, OES, surface wave probes, and QMS, we counted the absolute number of incident species (CF@sub x@, O, N, H, F, radicals and ions) that were dissociated and/or ionized in fluorocarbon plasmas. Next, we evaluated the surfaces of the various SiOCH films (k = 2.9-2.2) that had different film compositions and densities, and that had been exposed to various fluorocarbon plasmas. The etch rates, selectivity, and thicknesses of the surface polymers were analyzed. We found that the etch rates of the SiOCH films depended on both the "total number of F atoms in all of the incident CF@sub x@ reactive species", and "the surface reaction probability, which depends on ion energy". Lower oxygen concentrations in SiOCH film induce a narrower process window because the fluorocarbon polymer became thicker, even during lower incident CF@sub x@ flux conditions.@footnote 1@ As a result, the etch rate became very sensitive to changes in the incident CF@sub x@ fluxes, resulting a narrow process window for etching SiOCH and porous SiOCH materials. To ensure reliable interconnects for 45 nm and beyond, we require new technologies to realize both "quantitative control" and "instant stabilization" of the plasma parameters. Furthermore, we also need to develop a model to control the atomic layer modification (etching and/or degradation) of the actual etched surface for various materials. Cooperation between etching and other unit process engineers must be promoted in order to create a more reliable process module. @FootnoteText@ @footnote 1@ T.Tatsumi et al, Proceedings of the 2003 IITC (2003) 239.

2:40pm **PS+MS-TuA5 Plasma Etch Challenges for 45 nm Node and Beyond***, **R. Wise,*** IBM **INVITED**

Many novel technologies are candidates for introduction at the 45 nm technology node. Metal gate electrodes, high-k gate dielectric materials, hybrid oriented transistors (HOT), FINFET transistors, new silicide materials, multiple stressed liners, fully-silicided gates, and porous low-k BEOL materials are all currently under evaluation for introduction at the 45 nm node. The anticipated impact of each of these technology components on requirements of dry etch process and tooling is discussed in detail. Lithographic limitations will continue to require dry etch processes (e.g. gate, contact) to provide additional CD reduction to meet designed groundrules. These processes will include extension of well-known resist trim techniques as well as other techniques, such as providing a controllable taper through a sacrificial masking material. Available resist material will be reduced both by limitations of the lithographic process window (N.A , DOF, resolution) as well as implementation of multiple exposure techniques. These reductions in the available mask thickness required to preserve lithography process window have driven the need for highly selective etch processes, generally at the expense of uniformity (especially on 300 mm wafer sizes), defectivity, and profile of the transferred pattern. Later generation lithographic materials are expected to continue to exhibit increased sensitivity to line edge roughness. Process and tooling needs required to address these lithographic challenges are discussed.

3:20pm **PS+MS-TuA7 Invited Panel - "Challenges for 45 nm Node"***, C. Gabriel,* AMD (damage)*; M. Hussein,* Intel (scaling)*; C.-J. Kang,* Samsung (dielectric etch)*; S. Wege,* Infineon (silicon etch)

Panelists will present 5-minute perspectives.

3:40pm **PS+MS-TuA8 Discussion - "Challenges for 45 nm Node" Panelists and Attendees***,*

Plasma Science and Technology
Room 213B - Session PS2-TuA
Plasma and Polymers

Moderator: L.J. Overzet, University of Texas at Dallas

1:20pm **PS2-TuA1 Plasmas, Polymers and Plasma-deposited Polymer-like Films: Plasma Diagnostic Studies for SiO@sub 2@-like Film Deposition***, M. Creatore,* ***M.C.M. van de Sanden,*** Eindhoven University of Technology, The Netherlands **INVITED**

Low temperature plasmas for polymer modification and synthesis of polymer-like films are technologically appealing because of the development of plastic-based applications and the versatility of plasmas as processing tool in engineering the polymer-like film. As plasmas invade hot topics such as flexible electronics and nano-scale devices, the plasma-based technology urgently needs the support of fundamental studies, which can unravel the mechanisms of plasma-polymer interactions and deposition of polymer-like films. A valid example is the deposition of SiO@sub 2@ barrier layers on polymers for long-term stability devices, such as plastic windows, polyLEDs and TFTs: here the requirement of water vapor permeability is more demanding that in food packaging. This involves issues, such as the development of an interphase and the generation of defects during film growth, which go beyond the recipe for a stoichiometric, dense SiO@sub 2@ layer. Another example is the deposition of SiC@sub x@H@sub y@O@sub z@ polymer-like films as low-k dielectrics for ULSI technology. Highlighting the monomer dissociation paths is not only useful in controlling the carbon content in the film and, therefore, the quality of the dielectric, but it is also expected to pave the way towards the engineering of ultra-low-k materials. This contribution describes, through the chosen model system of SiO@sub 2@ and SiC@sub x@H@sub y@O@sub z@ film deposition, studies performed in an Ar-fed remote expanding thermal plasma where O@sub 2@ and hexamethyldisiloxane are injected downstream. The monomer dissociation paths controlled by the (Ar@super +@, e@super -@) flow emanating from the plasma source will be discussed in view of the results obtained by Cavity Ring Down Spectroscopy and Triple Stage Threshold Ionization Mass Spectrometry. Implications of these outcomes on the plasma-deposited film properties will be also addressed.

2:00pm **PS2-TuA3 Deposition of SiOx Films from Organosilicone and Oxygen Plasma under Continuous and Pulsed Modes***,* ***S.R. Kim,*** Chungju National University, Korea, South Korea

RF plasma enhanced chemical deposition were applied to get SiO@sub x@ on polymeric substrates with various processing conditions, such as input power, monomer/oxygen feed ratio, modulated frequency and duty cycle. Organosilicones were used as feed monomer and oxygen was used as mixing gas. Input power was varied from 50 to 300 Watt. Chemical bonding information of deposited film by FTIR-ATR shows that the absorption peak of Si-O near 1032 cm@super -1@ moved toward 1066 cm@super -1@ and Si-CH@sub 3@ peak was decreased as oxygen amount was increased. I-V curves from Lanmuir Probe was used to measure electron temperature, electron density and plasma potential. Optical Emission Spectroscopy (OES) was used to measure the plasma species and intensity of species and to obtain plasma pathway. Plasma density was of 4 x 10@super 8@ [cm@super -3@] and electron temperature of 2.8 eV and maximum deposition rate was 640 Å/min at 150 Watt. Plasma parameters, such as electron temperature, electron density, plasma potential, and plasma species were correlated to the properties of deposited films.

2:20pm **PS2-TuA4 Electron Impact Reactions of DVS-BCB Monomer in He Plasma for Low-k Film Deposition***,* ***K. KINOSHITA****, M. SHIMOYAMA, A. NAKANO, J. KAWAHARA, N. KUNIMI, T. KIKKAWA,* Mirai, Japan

DVS-BCB (divinylsiloxane-bis-benzocyclobutene) is known as a precursor of a spin-on low-k material with the dielectric constant of 2.7@footnote 1@. Plasma polymerization process has also been developed to deposit DVS-BCB film from the monomer@footnote 2@. Higher thermal stability (400 °C) and very thin (<20 nm) conformal film formation have been achieved by this vapor phase deposition technique. However, reactions of DVS-BCB in the plasma remain unclear. Recently, in-situ quadrupole mass spectrometry (QMS) study of this plasma showed that there were two types of unique reactions which had never been observed in the thermal polymerization process@footnote 3@. These were hydrogen attachment to and methyl group desorption from the DVS-BCB, resulting in different polymer structures from those of thermally polymerized films. This paper reports molecular orbital calculations for these reactions. Total MO energy calculated by the density functional technique with the 6-31G* basis set clearly showed that both the neutral DVS-BCB and ionized DVS-BCB were stabilized by the hydrogen attachment. The attachment energies are about 2 eV and 4 eV for neutral and ionized species, respectively. The methyl group desorption was also analyzed by changing the Si-CH@sub 3@ distance. When the Si-CH@sub 3@ distance d was stretched from the stable position (d=1.88 Å), there appeared two types of saddle point structures at d=2.38 - 3.88 Å before final dissociation. The total MO energy at this final condition showed a lower value than the transition state. This means, methyl group desorption reaction needs activation to proceeds. The MO calculations well explain the QMS observations. This work was supported by NEDO. @FootnoteText@ @footnote 1@ T. M. Stokich, Jr., et al.: Mat. Res. Soc. Symp. Proc., 227, (1991) 103.@footnote 2@ J. Kawahara, et al., Technical Dig. IEDM 2003, 6-2-1, (2003) 143.@footnote 3@ K. Kinoshita, et al., Proc. Dry Process Symp. 2003, 6-6, (2003) 157.

2:40pm **PS2-TuA5 Molecular Dynamics Study of Interactions Between Organic Polymer Surfaces and Hydrogen/Nitrogen Radical Beams***,* ***H.Y. Yamada,*** Kyoto University, Japan*; S.H. Hamaguchi,* Osaka University, Japan

We have studied atomistic scale interactions between organic polymer surfaces and beams obtained from hydrogen/nitrogen plasmas, using classical molecular dynamics (MD) simulations. In typical etching processes of low-dielectric-constant (i.e. low-k) organic polymer layers for semiconductor interconnect applications, hydrogen and nitrogen based plasmas are often employed as their plasma etching sources. To carry out MD calculations of such systems, we have developed a classical interatomic potential model for systems consisting of H, C and N atoms, using interatomic potential data obtained from quantum mechanical calculations. One of the key factors that allow us to appropriately handle various covalent bonds formed among C and N atoms in numerical simulations is an algorithm that we have developed to determine the order of each covalent bond automatically based on local atomic arrangement. In this presentation, we shall discuss details of the newly developed potential model as well as sample MD simulations. As to MD simulations, we have focused on plasma etching of low-k organic polymer surfaces and simulated interactions of such polymer surfaces with energetic radical/cluster beams containing N and/or H atoms. The results obtained from these MD simulations are also compared with recent experimental observations as well as previously obtained MD simulation results for hydrocarbon beam injections into organic polymer surfaces [H. Yamada and S. Hamaguchi, J. Appl. Phys. (2004), submitted.]. We have observed that, as in the case of carbon beam injection simulations, injected N atoms strongly react with the polymer substrate and form bonding networks of C and N atoms on the substrate surface. On the other hand, at similar low injection energies, N2 molecules are less reactive due to their strong covalent bonds. At higher injection energies, however, we have observed that more N molecules can break into N atoms and form bonding networks on the polymer substrate.

3:00pm **PS2-TuA6 Computational Investigation of the Role of Polyatomic Ions in Plasma Polymer Deposition***, I. Jang, W.-D. Hsu,* ***S.B. Sinnott,*** University of Florida

Fluorocarbon plasmas are widely used to chemically modify 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. For this reason, the deposition of mass selected fluorocarbon ions are useful for isolating the effects specific to polyatomic ions. In this study, the detailed chemical modifications that result from the deposition of beams of polyatomic fluorocarbon ions (C@sub 3@F@sub 5@@super +@ and CF@sub 3@@super +@) on polystyrene surfaces at experimental fluxes are identified using classical molecular dynamics simulations with many-body empirical potentials. The ions are deposited at incident energies of 50 or 100 eV/ion. For CF@sub 3@@super +@ deposition, F atoms play the most important role in fluorinating the polystyrene surface, as the majority of F atoms are covalently attached to the polymer chains through replacement of native H atoms or capping the ends of broken chains. CF@sub 2@ fragments are also an important long-lived species. In contrast, F atoms are a minor bi-product and CF@sub 2@ fragments are the most dominant species for C@sub 3@F@sub 5@@super +@ deposition on polystyrene. Thus the simulations explain the experimental finding that C@sub 3@F@sub 5@@super +@ is more efficient at producing fluorocarbon thin films. In particular, many larger fragments produced by C@sub 3@F@sub 5@@super +@ ion deposition contain more than one C atom, may have more than one active site, and readily react to grow polymer-like structures. In contrast, F atoms, the most dominant fragment in CF@sub 3@@super +@ deposition, effectively deactivate potential film nucleation sites when they fluorinate the polymer surface. We compare these findings to results for the deposition of comparable hydrocarbon ions (C@sub 3@H@sub 5@@super +@ and CH@sub 3@@super +@). This work is supported by the National Science Foundation (CHE-0200838).

3:20pm **PS2-TuA7 Study of the Selected Effect of Molecules Generated in N@sub 2@ and O@sub 2@ Plasma for the Surface Modification of HDPE, PVDF and PTFE.***, N. Vandencasteele,* Universite Libre de Bruxelles, Belgium*; A. Wagner,* Ames National Laboratory*; H. Fairbrother,* Johns Hopkins University*; **F. Reniers,*** Universite Libre de Bruxelles, Belgium

Although plasma treatments of polymers are widely used in today's industry, the surface modification mechanisms remain mostly unknown due to their complexity. The wide variety of the species generated in a plasma, combined with the specificity of a usual polymer surface make such reactions hard to understand. We have undertaken a global systematic study of the individual and synergetic effects of the species generated in a plasma on the surface modification of a series of model polymers: HDPE, PVDF, PTFE, as they illustrate the transition between C-H and C-F bonds. A modified RF plasma allowing to filter out some of the species was used@footnote 1@, as well as an in situ ion gun and a radical source. N@sub 2@ and O@sub 2@ plasmas were used, and the selected effect of N@sub2@@super +@/N@super +@, O@sub 2@@super +@/O@super +@ and O on the polymers was studied. Samples were characterized using water contact angle (WCA), AFM and XPS. The spatial distribution of the plasma species was analysed by OES. In our configuration, most of the particles reaching the polymer are neutrals and electrons. Results show that the nature and amount of the functionalities grafted, the roughness and the WCA strongly depend on the starting polymer, and on the nature of the incident beam. For instance, the functions grafted on HDPE using the plasma neutrals are mostly C=N groups, whereas nitrogen ion treatment leads to a majority of amines. The N@sub 2@ plasma treatment of PTFE induces defluorination of the polymer, with rapid increase of the nitrogen content. New chemical functions, and CF@sub 3@ groups are evidenced. The decrease of the WCA is directly correlated to the surface amount of nitrogen. On the contrary, exposure of PTFE to N ions leads to no significant grafting. Oxygen treatment of HDPE and PVDF lead to an increase of surface energy, but on PTFE a super-hydrophobic surface is created. @FootnoteText@ @footnote 1@ A. Wagner, D.H. Fairbrother, F. Reniers, plasma and polymers, 8 (2003) 119.

3:40pm **PS2-TuA8 Deposition of Plasma Polymer Coatings on Stainless Steel***, **A. Mistry,*** University of Sheffield, UK, U.K.*; F.R. Jones,* University of Sheffield, UK*; D.B. Hammond, T.H. English,* Corus Plc. Rotherham, UK

Plasma polymerisation is being investigated to produce coatings imparting a specific function on the surface of stainless steels, such as improved cleanability. One approach to this goal is through deposition of inorganic oxide layers that enhance the hydrophilicity of the surface, improve water run-off properties and enhance the surface's dirt shedding properties. Preliminary work with hexamethyldisiloxane (HMDSO) and titanium containing organo-metallic monomers, e.g. titanium (IV) isopropoxide, as the precursor with/without O@sub 2@ as a co-reactant for plasma polymerisation onto stainless steel has shown the potential of this approach. The results from XPS indicate that as the concentration of O@sub 2@ in the plasma increases, the species deposited on the surface incorporate less carbon. There is also a decrease in the measured contact angle, i.e. the surface becomes more hydrophilic. This change in surface chemistry to a more oxide-like state is shown by an increase in O:Metal ratio. Thus, the surface chemistry can change from organic polymeric-like at high monomer concentration and low power, to inorganic oxide-like at low monomer concentration and high power. The cleaning response of the coated surfaces has been investigated, and copolymerisation of these two monomers to impart other synergistic effects is being carried out.

Semiconductors
Room 304C - Session SC-TuA

Semiconductor Heteroepitaxy and Nanostructures

Moderator: R.S. Goldman, University of Michigan

1:20pm **SC-TuA1 Lattice Mismatched Heteroepitaxy: Evolution and Revolution***, **E.A. Fitzgerald,*** Massachusetts Institute of Technology **INVITED**

The scientific understanding of lattice-mismatched epitaxy has lead to a third era in the applications of epitaxy. Epitaxy was applied in applications benefiting from lattice-matched materials, and has migrated to applications with mild lattice-mismatch, such as the SiGe HBT and the InGaAs pHEMT. Today, we are able to create relaxed lattice constants that have significant lattice-mismatch with respect to bulk substrate, and in turn use those lattice constants to create extremely high levels of strain in new and conventional materials. In this talk, we will review the general principles of strain-relaxed epitaxy and show how new SiGe templates on Si have extended the electron and hole mobility in SiGe materials to unforeseen enhancements. Such enhancements promise to increase the current drive in MOSFET transistors at a time when smaller transistors are losing their driving efficacy as scaling continues. We show that strained SiGe nanochannels are most likely shaping the vertical wavefunction of carriers, leading to the very high enhancements in mobility despite very high vertical fields. New structures that not only add strain but are further engineered for robust processing will be presented.

2:00pm **SC-TuA3 Strain Relaxation of MBE-grown Step-Graded Metamorphic InAsP Buffers on InP Substrates***, **M.K. Hudait,** Y. Lin, S.A. Ringel,* The Ohio State University

Step-graded metamorphic InAsP buffers grown on InP substrates to increase the substrate lattice constant are of interest to support a range of high-speed electronic and infrared optoelectronic devices. Recent work by our group has shown that grading the composition of the anion sublattice using InAsP buffers as opposed to the group-III cation sublattice using InAlAs buffers is advantageous for MBE growth for such applications since decoupling the growth rate from the composition control results in superior morphological and thermophotovoltaic device properties. Here, we discuss the strain relaxation properties of step-graded InAs@sub y@P@sub 1-y@ (y=0.32-0.4) buffers, representing a total misfit of ~1.1-1.2% with respect to InP. For this study, InAsP buffers were grown on both (100) and 2° off-cut (100) InP substrates under identical MBE growth conditions with an average grading rate of 20% As/μm. The relaxation of each layer within each buffer was measured along [1-10] and [110] directions using TAXRD to evaluate asymmetric relaxation and tilt relative to the initial substrate orientation. For both substrate types, the strain relaxation was found to be symmetric and greater than 90% for the top InAs@sub 0.4@P@sub 0.6@ layer. This indicates that @alpha@ ([1-10] direction) and @beta@ ([110] direction) slip systems have similar activation energies for dislocation nucleation. Moreover, a small epilayer tilt of ~20-190 arcsec was observed for both substrate orientations, which indicates that tilt generated by @alpha@ and @beta@ dislocations will be in proportion to the substrate offcut resolved in [110] and [1-10] directions, respectively. The relation between these observations and properties of group-V and group-III core dislocations will be made to optimize the growth of these buffers. Correlations with the strain relaxation properties, surface morphology and cross-sectional interface properties will also be made as a function of substrate misorientation.

2:20pm **SC-TuA4 Molecular Beam Epitaxy of High-quality Ge on Si by Self-directed "Touchdown" of Nanoscale Seed Pads Through a Thin SiO2 Layer***, Q. Li, D. Leonhardt, Y.B. Jiang, H. Xu, S.R.J. Brueck, S. Hersee, **S.M. Han,*** University of New Mexico

Growing a lattice-mismatched, dislocation-free epitaxial film on Si has been a challenge for many years. Herein, we exploit nanoheteroepitaxy to grow high-quality Ge epilayer on Si. A 1.2-nm-thick chemical SiO@sub 2@ film is produced on Si in a H@sub 2@O@sub 2@ and H@sub 2@SO@sub 4@ solution. When the chemically oxidized Si substrate is exposed to Ge molecular beam, relatively uniform-size nanoscale seed pads form in the oxide layer and "touch down" on the underlying Si substrate. Although the "touchdown" location is random, the seed pad growth is self-limiting to 7 nm in size. Upon continued exposure, Ge selectively grows on the seed pads rather than on SiO@sub 2@, and the seeds coalesce to form an epitaxial lateral overgrowth (ELO) layer. The Ge ELO layer is characterized by high-resolution, cross-sectional transmission electron microscopy (XTEM), Raman spectroscopy, and etch-pit density (EPD). The XTEM images reveal that the Ge ELO layer is free of dislocation network and that the epilayer is fully relaxed at 2 nm from the heterojunction. The Raman shift of Ge optical phonon mode exactly matches that of relaxed bulk Ge, further supporting that the ELO layer is fully relaxed. The XTEM images, however, show that stacking faults exist near the Ge-SiO@sub 2@ interface. A small fraction (~4x10@super -3@%) of these stacking faults propagate to the epilayer surface and form etch pits, when immersed in a solution containing HF, HNO@sub 3@, glacial acetic acid, and I@sub 2@. The resulting EPD is consistently less than 2x10@super 6@ cm@super -2@. The reduction of strain density near the Ge-Si heterojunction, leading to high quality Ge ELO layer, is mainly attributed to a high density (~10@super 11@ cm@super -2@) of nanoscale Ge seed pads interspaced by 2- to 12-

nm-wide SiO@sub 2@ patches. This "touchdown" technique may potentially enable growing other highly lattice-mismatched epilayers on Si, such as GaN and SiC.

2:40pm **SC-TuA5 Tuning of the Emission Wavelength of Self-assembled InAs/InP (001) Quantum Dots using Grown-in Defects and Ion Implantation***, **C. Dion,** N. Shtinkov,* École Polytechnique de Montréal, Canada*; S. Raymond,* Conseil National de Recherche du Canada, Canada*; M. Chicoine, F. Schiettekatte,* Université de Montréal, Canada*; P.J. Poole,* Conseil National de Recherche du Canada, Canada*; R.A. Masut, P. Desjardins,* École Polytechnique de Montréal, Canada

We have investigated the effect of post-growth rapid thermal annealing (RTA), grown-in defects, and ion implantation on the low temperature photoluminescence (PL) spectra of self-assembled InAs/InP(001) quantum dots (QD) grown by chemical beam epitaxy (CBE) and metal-organic vapor phase epitaxy (MOVPE) in order to develop a detailed understanding of the key diffusion mechanisms involved in such defect-mediated intermixing techniques. In untreated samples, blueshifts of up to 90 meV in the PL spectra are observed after RTA at 800 °C for 210s with no broadening of the emission peak. We attribute this thermally induced shift to the diffusion of group V atoms between the QD and the surrounding material. In order to promote interdiffusion and to obtain larger blueshifts, we have studied the effect of introducing point defects into an InP capping layer, far from the QD region, either by growing InP at low temperature or by implanting P atoms at doses ranging from 10@super11@ to 10@super 14@ ion/cm@super 2@. The introduction of grown-in defects results in a marked increased in PL shifts, which can reach up to 250 meV following RTA at 765 °C for 90 s, revealing that the excess of points defects in that layer promote interdiffusion in the QD region. Even more dramatic effects are measured in ion implanted sample for which significant blueshifts of 300 meV can be observed following anneals at temperatures as low as 400 °C. In order to quantify these effects, we carried out tight-binding calculations of the transition energies in thin diffused quantum wells. Experimental results for the emission of the wetting layer and our simulations indicate that ion implantation leads to an important reduction of the activation energy for As/P interdiffusion to values as small as 0.4 ± 0.2 eV.

3:00pm **SC-TuA6 Gated Si/SiGe Quantum Dots with Low Charge Noise***, **L.J. Klein**, S. Goswami, K.A. Slinker, K.L.M. Lewis, S.N. Coppersmith, D.W. van der Weide, M.A. Eriksson,* University of Wisconsin, Madison*; J.O. Chu, J.A. Ott, P.M. Mooney,* IBM, TJ Watson Research Center

The stability and noise affecting single electron charging in quantum dots fabricated in a Si/SiGe heterostructure are investigated. Electron beam lithography and subsequent reactive ion etching are used to define the quantum dot. The dot potential and electron density are modified by laterally defined side gates in the plane of the dot. Low temperature measurements (0.2 K) show Coulomb blockade with a single electron charging energy of 4 meV. The long term stability of the Coulomb blockade oscillations is determined in part by the number and stability of electrons captured in trap states in the vicinity of the quantum dot. Motion of this trapped charge modifies the dot potential and is detected as discrete shifts in the Coulomb blockade peak positions. Thermally annealing the sample (400C in Ar) after reactive ion etching reduces the charge noise from such trap states, allowing the acquisition of stable Coulomb diamond data over several hours. Tunnel-coupled double quantum dots have been fabricated and measured using similar techniques. The potential application of such Si/SiGe quantum dots for spin based quantum computation is discussed.

3:20pm **SC-TuA7 Blue Photoluminescence of Si Nano-crystallites Embedded in Silicon Oxide***, **G.-J. Kim**, J.H. Kim, K.A. Jeon, S.Y. Lee,* Yonsei University, Korea

Synthesis and luminescent characteristics of Si nano-crystallites are reported depending on deposition condition. Si nanocrystalline thin films on p-type (100) silicon substrate have been prepared by a pulsed laser deposition (PLD) technique using a Nd:YAG laser. The Si nano-crystallites with the average size of 2 nm are observed in the SiO@sub 2@ matrix. Strong blue photoluminescence has been observed at room temperature. The optical and structural properties of thin films have been investigated as a function of laser energy density, ambient gas pressure, annealing, and oxidation process. These results indicate that the blue photoluminescence of Si nano-crystallites is related to the quantum size effect of Si nanocrystallites.

3:40pm **SC-TuA8 Silicon Nanocrystal Formation in an Oxide Matrix: Chemical and Strain Effects***, **D. Yu**, G.S. Hwang,* The University of Texas at Austin

Nanocrystalline Si (nc-Si) embedded in an oxide matrix has received great attention due to its promising applications for advanced electronic and optical devices. The unique electrical and optical properties of oxide-embedded nc-Si appear to be strongly influenced by the crystallite size, shape, density, and oxide composition. It is therefore necessary to develop a detailed understanding of the nc-Si growth. We have developed a multiscale computational model for nc-Si synthesis in an oxide matrix by phase separation of silicon suboxide. This multiscale approach combines i) first principles quantum mechanics calculations of fundamental processes and ii) kinetic Monte Carlo simulations of long-time scale phase separation. Using the computational approach, we have identified formation mechanism of Si clusters in silicon suboxide. In this talk, first we will present fundamental processes involved in the phase separation including: i) Si interstitial behavior in an oxide and ii) O diffusion energetics which depends on strain and chemical environment. Based on these results, we will discuss the relative contribution of strain and suboxide penalty to the phase separation. Finally, we will present the process of Si particle formation, together with a comparison to experimental observations.

Surface Science
Room 210B - Session SS1-TuA
Hydrocarbon Reactions on Metal Surfaces

Moderator: D.E. Barlow, Naval Research Laboratory

1:20pm **SS1-TuA1 Thermodynamics and Kinetics of Elementary Steps on Surfaces, and their Applications in Modeling Complex Reactions***, **C.T. Campbell,*** University of Washington **INVITED**

Some useful concepts for describing elementary reaction steps on surfaces will be reviewed, and illustrated with example applications to catalytic reactions. First, the characteristics which define a true "elementary step" will be considered. In general, the reaction order is well defined for true elementary steps, and their prefactors can be theoretically estimated with reasonable accuracy using transition state theory and simple concepts of statistical mechanics. Once the prefactor is known, a single absolute rate measurement provides the activation energy, which is thus obtained with good accuracy even when the prefactor used is in error by two orders of magnitude. The net reaction energy often can be measured independently. Examples of doing this with adsorption calorimetry will be reviewed. Recent developments promise to make calorimetric measurements of adsorption energies on single crystal surfaces more common, since they now can be applied to crystals as thick as obtainable by simple mechanical thinning (80 ï⍰-m). Once the net reaction energy is known for an elementary step, a measurement of its activation energy directly provides that for its reverse step and, through knowledge of statistical mechanics, its equilibrium constant. These kinetic and thermodynamic parameters are invaluable in examining or modeling the rates of complex reaction mechanisms, which in general turn out to depend on the kinetic and thermodynamic parameters of only a few of the many elementary steps involved. A simple method for determining which of the elementary steps are critical, based on the â?odegree of rate controlâ?⍰, will be described. Work supported by DOE-OBES and NSF.

2:00pm **SS1-TuA3 Recent Advances in the Surface Chemistry of Hydrocarbon Fragments on Transition Metals***, **F. Zaera,*** University of California

A brief review of recent results from our efforts to elucidate the mechanistic details of the surface chemistry of hydrocarbons on transition metal surfaces will be presented. The chemistry of C4 hydrocarbons on Pt(111) single-crystal surfaces will be highlighted, with focus on the steps responsible for double bond migration and cis-trans isomerization in olefins. A comparison will be provided with our previous studies using shorter moieties, and the role of different key intermediates such as alkyls and allyls will be discussed. Insertion reactions will be addressed next. Specifically, the mechanism of chain growth on Ni(110) surfaces will be analyzed in terms of the chemistry of methylene and methyl on that surface. The effect of coadsorbed oxygen on these reactions, as well as the opening of new oxygen incorporation steps, will be discussed. Finally, reference will be made to the surface chemistry of chiral compounds on metals as it relates to enantioselective catalysis.

2:20pm **SS1-TuA4 Enantioselective Reactivity of R-2-bromobutane on Chiral Copper Surfaces***, **D.M. Rampulla**, A.J. Gellman,* Carnegie Mellon University

Enantioselective reactions are integral to most biological chemistry and large-scale pharmaceutical production. Enantioselective reactions require chiral media such as solvents, surfaces, or catalysts of a single handedness. Enantioselective heterogeneous catalysis is a promising method for the preparation of chiral compounds but requires catalytic surfaces with inherently chiral structure. The stepped and kinked high Miller index surfaces of metals are naturally chiral and have been shown to interact enantiospecifically with chiral adsorbates. Enantioselective desorption of small chiral molecules from such surfaces has been demonstrated and studied, but enantioselective reactivity on naturally chiral metal surfaces has not been explored. Temperature Programmed Reaction Spectroscopy (TPRS) has been used to study the decomposition of R-2-bromobutane on the chiral Cu(643)@super R@ and Cu(643)@super S@ surfaces. Alkyl halides, such as R-2-bromobutane adsorb dissociatively to form R-2-butyl groups, which decompose via @beta@-hydride elimination to yield 1- and 2-butenes. The temperatures at which these desorb and the selectivity to 1- and 2-butenes are influenced by the chirality of the copper surfaces. Earlier results of R-2-bromobutane on Cu(531)@super R&S@ surfaces will be discussed and compared with more recent results obtained on the Cu(643)@super R&S@ surfaces.

2:40pm **SS1-TuA5 Stereochemistry in Surface Explosion***, **K.-H. Ernst**, B. Behzadi, R. Fasel, S. Romer,* EMPA Duebendorf, Switzerland

The vast majority of chiral compounds crystallize into racemic crystals. It has been predicted early and was later experimentally established as a rule, that chiral molecules on surfaces are more easily separated into homochiral domains due to confinement into a 2D-plane and lower entropic contributions. We investigated the formation and stability of two-dimensional tartrate lattices on a Cu(110) surface for the racemic mixture by means of temperature programmed desorption (TPD), low energy electron diffraction (LEED), and X-ray photoelectron spectroscopy (XPS). At low coverage, the bitartrate species becomes separated into homochiral domains, but with increasing surface density the monotartrate species forms a closed-packed racemic 2-D crystal. Consequently, the 2-D conglomerate bitartrate phase does not show differences to the enantiopure bitartrate phase with respect to thermal stability. However, the thermally induced autocatalytic decomposition reaction, so-called surface explosion, of the monotartrate species is influenced by the chirality of the adjacent molecules. The racemic mixture undergoes decomposition at a lower temperature than the enantiopure lattice at same coverage and lateral arrangement. This is in contrast to the higher stability of 3D tartaric acid crystals, but is consistent with the observation that homochirality is preferred in hydrogen-bonded self-assembled biomolecular structures.

3:00pm **SS1-TuA6 The Ullmann Coupling Reaction: Atomic Scale Study of the Reactive Intermediates and Products of a Surface Catalyzed Reaction***, **S.U. Nanayakkara**, E.C.H. Sykes, L.C. Fernández-Torres, P. Han, P.S. Weiss,* The Pennsylvania State University

We present an atomic-scale study of the Ullmann coupling reaction on Cu{111} using low temperature scanning tunneling microscopy and spectroscopy. We have studied the reactive intermediates and the products of the Ullmann coupling reaction between bromobenzene molecules, which form biphenyl at room temperature (293 K). Chemical identification of the surface-bound species has been achieved using their tunneling spectroscopic signatures. We demonstrate that bromobenzene molecules dissociatively chemisorb at 293 K and form phenyl intermediates, which travel distances of up to a few 1000 @Ao@ over Cu{111} terraces to bind preferentially at step edges. This preference is due to the anisotropic electron density distribution at the step edges. We identify the surface step edge as the active site of this reaction on Cu{111} for C-C bond formation. Once two phenyl intermediates combine to form biphenyl, these product molecules diffuse onto the terraces and arrange as clusters. Our interpretations of the preferred adsorption sites and the intermolecular interactions of adsorbates are explained in terms of the local electronic perturbations on the surface by surface steps and adsorbates.

3:20pm **SS1-TuA7 Adsorption Energies of Small Alkane Molecules on MgO(100), Pt(111), and C(0001)/Pt(111) by Temperature Programmed Desorption***, **S.L. Tait, Jr.,*** University of Washington*; Z. Dohnálek,* Pacific Northwest National Laboratory*; C.T. Campbell,* University of Washington*; B.D. Kay,* Pacific Northwest National Laboratory

The adsorption of small hydrocarbon molecules at oxide and metal surfaces represents an important scientific problem with applications in catalysis and sensors. We have used molecular beams and temperature programmed desorption (TPD) to study the adsorption of small alkane molecules, C@sub n@H@sub 2n+2@ (n=1-10), on MgO(100), Pt(111), and a two-dimensional graphite film on Pt(111). Hydrocarbon molecules are deposited on the surface by a highly collimated molecular beam with a well-defined incident angle and kinetic energy. The adsorption energies and pre-exponential factors are extracted from TPD data. Simulations based on the results of this analysis show excellent agreement with experiment. The desorption prefactors increase with alkane chain length by more than five orders of magnitude over the range of alkane molecules studied. Adsorption energy on each surface increases linearly with alkane chain length with a y-intercept value near zero. Prior studies have found a non-zero intercept by treating the pre-exponential factor as constant with alkane chain length. This increase in pre-exponential factor can be attributed entirely to the increase in the rotational entropy in the transition state theory, assuming that the adsorbed initial state is not a free rotor but that the transition state is. Pacific Northwest National Laboratory is a multiprogram National Laboratory operated for the U. S. Department of Energy by Battelle Memorial Institute under contract DE-AC06-76RLO 1830. SLT supported by a UW/PNNL Joint Institute for Nanotechnology fellowship.

3:40pm **SS1-TuA8 Characterization of Ethylidene and Methylidyne on Pt(111) with Infrared Spectroscopy***, **R. Deng**, E. Herceg, M. Trenary,* University of Illinois at Chicago

Hydrocarbon intermediates formed in the adsorption and decomposition of ethylene (C@sub 2@H@sub 4@), diiodomethane (CH@sub 2@I@sub 2@) and iodomethane (CH@sub 3@I) on Pt(111) were investigated using reflection absorption infrared spectroscopy (RAIRS) and mass spectrometry. The ethylidene (CHCH@sub 3@) species is identified on the basis of RAIRS peaks at 2960 cm@super -1@ and 1387 cm@super -1@ that are assigned to the CH@sub 3@ asymmetric stretch and the CH@sub 3@ symmetric bend, respectively. It is found that the highest ethylidene coverage can be produced by ethylene exposure to the surface at temperatures around 280 K. Ethylidene undergoes rapid hydrogenation upon exposure to 2x10@super -7@ Torr of H@sub 2@ at 250 K to produce gas phase ethane, as detected by a mass spectrometer. The results indicate that ethylidene could be an intermediate in ethylene hydrogenation on transition metal surfaces near room temperature. Surface methylidyne can be formed in multiple ways: thermal decomposition of diiodomethane and iodomethane; ethylene decomposition at a temperature of about 500 K; and surface carbon hydrogenation. Methylidyne is identified by a CH (CD) stretch mode at 2956 (2206) cm@super -1@. The co-adsorption of surface hydrogen and iodine causes this band to shift to higher frequency. The observation of methylidyne at 500 K indicates that C-C bond scission of the initially adsorbed ethylene occurs at this temperature.

Surface Science
Room 210C - Session SS2-TuA

Welch Award Symposium: Nucleation and Growth

Moderator: P.J. Feibelman, Sandia National Laboratories

1:20pm **SS2-TuA1 Real-Time Microscopy of Second Order Phase Transitions on Pb/Ge(111)***, **Y. Sato**, S. Chiang,* University of California, Davis

Using the Low Energy Electron Microscope (LEEM), we have studied phase transitions that occur on the Pb/Ge(111) surface. We have observed a very unusual second order phase transition with strong fluctuations at coverages above 1ML. The Pb layer forms two stable (@sr@3x@sr@3)R30° phases on the surface, a low-density @alpha@ phase and a dense @beta@ phase. It is well known that the critical temperature of the phase transition from @beta@ to (1x1) depends strongly on the coverage. The transition occurs at 180C for coverage below 1ML and at 270C for coverages above 1.33ML. LEEM data clearly show this difference in the critical temperature derives from the different mechanisms of the transformation. For coverages between 0.33ML and 1ML, where the @alpha@ phase coexists with the @beta@ phase below the critical temperature and with the (1x1) phase above it, the reversible phase transformation from @beta@ to (1x1) shows typical second order phase transition behavior, i.e., the intensity of the @beta@ phase gradually changes with temperature. On the other hand, for coverages above 1 ML, where the surface is either the low temperature @beta@ phase or the higher temperature (1x1) phase, the system shows an unusual second order phase transition. As the sample is heated through the critical temperature, the (1x1) phase appears as small domains over the surface. The domains appear and disappear until they are stabilized in the new phase. The transition is reversible, and similar behavior is observed upon cooling. The frequency analysis of the critical fluctuations will be presented, and the different mechanisms for both of the second order phase transitions mentioned above will be discussed.

1:40pm **SS2-TuA2 Dislocation-Driven Surface Dynamics on Solids*, S. Kodambaka,*** *S.V. Khare, J. Bareno, W. Swiech, I. Petrov, J.E. Greene,* University of Illinois at Urbana-Champaign

Using low-energy electron microscopy, we investigate the near-equilibrium dynamics of surface-terminated dislocations. We observe, in real time, the thermally-driven (1500-1700 K) nucleation and shape-preserving growth of spiral steps rotating at constant temperature-dependent angular velocities (@omega@(T)) around cores of dislocations terminating on TiN(111) in the absence of applied external stress or net mass change. We measure @omega@ as a function of spiral geometry, N@sub2@ partial pressure, annealing time, and temperature. We find that @omega@ is independent of the local environment and ambient, and decreases linearly with time. From the temperature-dependent @omega@ data, we obtain an activation barrier of 4.9±0.3 eV for the growth of spirals. This phenomenon, attributed to point-defect migration from the bulk to the surface along dislocation lines, is both qualitatively and quantitatively different from step curvature-driven surface dynamics and "standard" Burton-Cabrera-Frank (BCF) spiral growth.@footnote 1@ Our results demonstrate that dislocation-mediated surface roughening can occur even in the absence of deposition or evaporation, and provide fundamental insights into mechanisms controlling nanostructural stability. We expect that this process is general and that it occurs in other materials.@footnote 1@ S. Kodambaka, S.V. Khare, W. Swiech, K. Ohmori, I. Petrov, and J.E. Greene, Nature, May 6th issue, 2004.

2:00pm **SS2-TuA3 Probing the Kinetics of Nanoscale Self-Assembly on Surfaces*, G.L. Kellogg,*** Sandia National Laboratories, US **INVITED**

Pb atoms deposited on Cu(111) form a Pb-poor surface-alloy phase and a Pb-rich overlayer phase which spontaneously order into nanoscale domain patterns.@footnote 1@ The thermodynamic forces responsible for the self-assembly have been determined in previous studies with the LEEM.@footnote 2@. In this talk I will describe recent studies of the atomic mechanisms underlying the remarkable cooperative motion that allows these patterns to form and evolve. For example, the ordering of Pb overlayer islands occurs by islands containing 10's of thousands of atoms moving 100's of nm's is a few minutes. To help understand the atomic processes responsible for such motion, we measured the thermal decay of pure Cu, Pb-overlayer, and Pb/Cu surface-alloy islands using both STM and LEEM.@footnote 3@ The results indicate that the diffusion of Cu atoms over the Pb-Cu surface alloy is rate-determining for the decay both Pb overlayer and Pb-Cu alloy islands and that slower diffusion on the surface alloy is due to path blocking by embedded Pb atoms. Additional LEEM studies of Cu island nucleation within the Pb overlayer strongly suggest that the large-scale mobility of overlayer islands is accomplished by fast migration of Cu atoms within the overlayer. Thus, the rapid self-assembly in this system can, surprisingly, be traced to the existence of a low energy Cu thermal defect within the Pb overlayer. Sandia is operated by Sandia Corporation, a Lockheed Martin company, for the U. S. Department of Energy under Contract #DE-AC04-94AL85000. @FootnoteText@ @footnote 1@ R. Plass, J. A. Last, N. C. Bartelt, and G. L. Kellogg, Nature 412, 875 (2001).@footnote 2@ R. van Gastel, R. Plass, N. C. Bartelt, and G. L. Kellogg, Phys. Rev. Lett. 91, #55503 (2003); R. van Gastel, N. C. Bartelt, P. J. Feibelman, Francois Leonard, and G. L. Kellogg, Phys. Rev. B, submitted.@footnote 3@ M. L. Anderson, N. C. Bartelt, P. J. Feibelman, G. L. Kellogg, and B. S. Swartzentruber, in preparation.

2:40pm **SS2-TuA5 Medard Welch Award Presentation: Growth and Epitaxy of Thin Pentacene Films*,*** **INVITED**

Pentacene (Pn) is the highest mobility organic semiconductor known. It is a crystalline organic solid that can be deposited on a substrate by either vacuum sublimation, or by spin coating of a suitable soluble precursor followed by mild annealing. In this talk I will focus on studies of Pn thin film growth in vacuum, studies by in-situ Low Energy Electron Microcopy, Scanning Tunneling Microscopy, and Photo Electron Spectroscopy. We find that the molecular orientation in the growing film, as well as the nucleation density depend strongly on the choice and preparation of the substrate. For instance, grain sizes can vary from 0.1 micrometer to over 0.1 millimeter. Molecules can orient in-plane or out-of-plane, depending on the electronic structure of the substrate. On most substrates, grains show random azimuthal orientation, but recently we have succeeded in growing epitaxial pentacene films on a number of different substrates that hold promise for the fabrication of epitaxial organic thin film transistors with improved transport properties. In this talk I will review our results and recent progress.

3:20pm **SS2-TuA7 Growth Dynamics of Organic Semiconductors*, F. Schreiber,*** Oxford University, UK **INVITED**

We will review our recent work on the growth dynamics of molecular semiconductors by organic molecular beam deposition (OMBD), with emphasis on growth studies beyond the first monolayer, i.e. the evolution of the film structure and morphology. After briefly discussing general issues related to growth modes, correlation functions, dynamic scaling, and growth exponents, we will try to identify the general features that distinguish organic from inorganic systems, such as the different interaction potentials and the internal degrees of freedom of organic molecules.@footnote 1@ We will then discuss selected case studies of perylene-derivatives (in particular diindeno-perylene (DIP)@footnote 2@ and 3,4,9,10-perylenetetracarboxylic dianhydride (PTCDA)@footnote 3@), with results on the dynamic scaling exponents and real-time studies of the growth. Finally, we will briefly discuss the implications for organics-based heterostructures and the improvement of device performance. @FootnoteText@@footnote 1@F. Schreiber, Phys. Stat. Sol. (a) 201 (6) (2004) 1037 @footnote 2@A. C. Dürr et al., Phys. Rev. Lett. 90 (2003) 016104 @footnote 3@B. Krause et al., Europhys. Lett. 65 (3) (2004) 372

Thin Films
Room 303C - Session TF+NS-TuA
Focused Beam Processing & Fabrication

Moderator: J.M. Fitz-Gerald, University of Virginia

2:20pm **TF+NS-TuA4 Localized Heating Effects During Electron Beam-Induced Deposition of Nanostructures*, S. Randolph,*** *J.D. Fowlkes, P.D. Rack,* University of Tennessee, Knoxville

In recent years, electron beam-induced deposition (EBID) has shown promise for use in next-generation lithography applications and nanostructure fabrication. While many materials have been successfully deposited on various substrates by EBID, control of feature size and geometry has been lacking. One possible mechanism that makes process control problematic is the localized heating that occurs in the nanostructure while undergoing constant electron bombardment. While the electron beam-induced heating of a bulk sample in the typical SEM is negligible, a focused beam projected onto a raised high aspect ratio feature can cause significant temperature rises in the feature. As the sticking coefficient and residence time of the impinging precursor gas are strong functions of the substrate temperature, it is expected that the deposition rate will vary with the surface temperature of the nanostructure if the process is mass transport limited. Assuming that there are no radiative and convective heat losses through the surface of the sample, the nanostructure growth creates a quasi one dimensional structure that does not dissipate heat as well as a bulk film. Consequently, as the nanostructure grows the surface temperature increases thereby reducing the sticking coefficient and residence time of the impinging gas. In this presentation, a Monte-Carlo electron-solid model will be illustrated which calculates the energy deposition profiles in the bulk and nanostructured features. Using these profiles, a finite element model is used to calculate the temperature profiles. Bulk and nanostructured features will be compared and discussed in context with experimentally observed growth rates.

2:40pm **TF+NS-TuA5 Electron Beam Micromachining*, P.E. Russell,*** *D.P. Griffis, A. Garetto,* NC State University **INVITED**

While chemically enhanced focused ion beam micromachining (CE-FIBM) or other ion based micromachining techniques have many practical applications, any ion beam based micromachining technique typically results in some degree of sample damage as well as residual implanted ions. In many cases, these implanted ions cause deleterious effects such as staining in the case of mask repair, alteration of the electrical characteristics of semiconductor and optoelectronic samples and/or surface damage in samples prepared for high resolution electron microscopy or microanalysis. In order to avoid ion staining and following up on our earlier efforts in electron beam induced deposition and material removal, our efforts are currently focused on gaining increased understanding of and development of chemically enhanced electron beam micromachining (CE-EBM) of technologically important materials. The interaction of incident and emitted (secondary and backscattered) electrons with surfaces in the presence of a suitable chemical precursor can induce useful chemical reactions. Electron beam energies from a few hundred eV to 30 keV are routinely available on scanning electron microscopes, and a few systems allow much lower beam energy. The magnitude of the emission of secondary electrons peaks in the range of a few eV to tens of eV's while backscattered electrons are emitted over a broad, albeit higher range of energies up to the full primary energy. This wide range of electron energies coupled with the richness of possible beam/sample/precursor interactions makes available a wide range of possibilities for both deposition and etching with, when compared to damage resulting from ion beam exposure, a dramatically reduced probability of damage and/or unintentional alteration of samples. This talk will review recent developments in both the application and understanding of CE-EBM.

3:20pm **TF+NS-TuA7 Nanoscale Structures and Devices Produced Using Energetic Atomic Beams***, **E.A. Akhadov,*** Los Alamos National Laboratory*; D. Read,* Florida State University*; A.S. Cavanagh, A.H. Mueller,* Los Alamos National Laboratory*; J.C. Gregory, G.P. Nordin,* University of Alabama in Huntsville*; M.A. Hoffbauer,* Los Alamos National Laboratory

Nanoscale patterning of polymeric materials and low temperature thin film growth become possible using atomic species with kinetic energies similar to chemical bond strengths. We have developed a technique exclusive to LANL, called Energetic Neutral Beam Lithography/Epitaxy (ENABLE), that utilizes energetic neutral atoms for materials processing at the nanoscale. In this presentation, we demonstrate the use of atomic oxygen for nanoscale polymer etching and atomic nitrogen for templated nitride thin film growth. High-precision nanoscale formations (<50nm) with aspect ratios exceeding 35:1 were fabricated in polymer films. Taking advantage of the low temperature thin film growth afforded by ENABLE, we have fabricated AlN-based structures using pre-etched polymeric templates for potential electronic, photonic, and nanofluidic applications.

3:40pm **TF+NS-TuA8 A Three - Dimensional Computer Simulation of Electron - Beam Induced Deposition (EBID)***, **J.D. Fowlkes,** P.D. Rack, S. Randolph,* University of Tennessee, Knoxville

A simulation will be presented of the electron - beam induced deposition (EBID) process that was coded using the Matlab(R) program. The simulation has a Monte Carlo component to predict electron trajectories as well as elastic and inelastic electron â?" substrate interactons. A discretization scheme projects each electron scattering event onto a three dimensional matrix to provide a reference point to test for a host of possible events per matrix node including secondary electron generation and/or EBID. Three phases coexist in the matrix including the precursor gas, the deposited phase and the substrate phase. A dynamic model tracks the gas - surface interaction including precursor adsorption, deposition and desorption under thecontext of a Langmuir type surface coverage. Primary, backscattered, and secondary electrons that escape the gas - pillar and gas - substrate interface may induce deposition based on their trajectory, energy and precursor surface coverage. The probability of EBID is based on a "shifted and scaled" ionization cross-section for the precursor gas molecule to be roughly applied as a dissociation cross - section. Primary (PE) and secondary electrons (SE) contribute most signficantly to the EBID growth of high-aspect ratio nanopillars while backscattered electrons (BSE) play more of a feature coarsening role. Two regimes of pillar growth are observed; a region characterized by linear a growth rate where the electron interaction volume interacts with both the growing pillar and the substrate and a second regime, again linear in growth rate, whereby the penetrating electrons interact solely with the high aspect pillar.

Vacuum Technology
Room 303D - Session VT-TuA

Special Session at the 51st International AVS Symposium: "Fleming Centenary Session: The Birth and Evolution of Electronics"

Moderator: R. Langley, Oak Ridge Science Consultants

1:20pm **VT-TuA1 John Ambrose Fleming and the Beginning of Electronics***, **H.F. Dylla,*** Jefferson Laboratory **INVITED**

This year is the centenary of John Ambrose Fleming's momentous patent on the thermionic diode that was the birth of electronics. The "Edison effect" was discovered in 1882, this was later shown to be the result of thermionic emission of electrons from a heated filament into a vacuum. Edison did not make any significant devices based on this discovery and the effect was ignored for more that 8 years. In 1890 Fleming explained the effect and showed that the thermionic diode could be used as a rectifier. Fourteen years later Fleming filed this momentous 1904 patent on the thermionic diode that was the first public announcement of the electron tube; this revolutionized the development of radio and led to the invention of the thermionic triode by Lee de Forest in 1906. The background to these events will be described.

2:00pm **VT-TuA3 Vacuum and the Electron Tube Industry***, **P. Redhead,*** National Research Council, Canada **INVITED**

The electron tube industry started with the patenting of the thermionic diode by John Ambrose Fleming in 1904. In the beginning the vacuum technology used by the infant tube industry was copied from the existing technology of the incandescent lamp industry. The growing demands for electron tubes for military and naval communications in the first world war led to major improvements in pumps and processing methods. By the 1920s the tube industry was developing mass production methods of processing to satisfy the demands for receiving tubes by the burgeoning radio industry. Further expansion of the tube industry in the 30s and 40s led to improvements in automatic equipment for processing vacuum tubes leading to the massive production rates of electron tubes in the second world war. The demands of radar during the war resulted in the development of techniques for large-scale production of microwave tubes and CRTs, the latter technology being put to good use later in TV picture tube production. The requirements of the electron tube industry dominated the vacuum industry for about 30 years until the introduction of the transistor. The developments in vacuum technology in the electron tube industry will be reviewed.

2:40pm **VT-TuA5 The Science and Technology of Pumping Residual Gases in Vacuum Tubes***, **B. Ferrario,*** Saes Getters SpA, Italy **INVITED**

Since the invention of the vacuum oscillation valve by Fleming impressive developments have been made in the field of vacuum tubes and related applications. Vacuum tubes are nowadays widespread devices in spite of the introduction of the transistors as substitutes for the vacuum valves; here they are referred to as a large family of products which has been growing along many decades and include, for example, power vacuum tubes, x-ray tubes, CRTs for black&white and color television, and the more recent so called "thin CRTs", i.e. Field Emission Displays (FED).Vacuum science and technology have been playing an essential role in these developments and have evolved symbiotically with them, often generating fundamental knowledge useful for many other vacuum related applications. The evolution of the vacuum tube family has required an increasing degree of vacuum and longer lifetimes along with more and more cost effective manufacturing processes; particular attention has therefore been drawn on the phenomena which are responsible for vacuum deterioration after seal-off , among which outgassing is usually the most relevant. This has made the study of outgassing phenomena , the residual gas analysis, the selection of the appropriate materials and the optimization of the manufacturing processes increasingly important. Concurrently, important developments have been made concerning getters which, after seal-off, act as in situ pumps to countermeasure the outgassing effects; indeed they are used, in various materials and configurations, to minimize the total residual pressure and particularly the partial pressures of the so called "active" gases (H@sub 2@O, CO@sub 2@, H@sub 2@, O@sub 2@, etc.) which are usually most detrimental and account for most of the total pressure in vacuum tubes.This paper reviews the issues related to residual gases in vacuum tubes and the early as well as especially the modern getter solutions developed to ensure the desired residual gas pumping in various vacuum tube types.

3:20pm **VT-TuA7 Vacuum Microelectronic Devices and Vacuum Requirements***, **G.E. McGuire**, O.A. Shenderova, T. Tyler,* International Technology Center **INVITED**

With the emergence of microfabrication and thin film deposition techniques developed by the semiconductor industry, it became apparent that miniature vacuum microelectronic devices could be developed. Using approaches as diverse as controlled evaporation, chemical etching (both wet isotropic and anisotropic and dry plasma etching) and controlled oxidation, sharp tips were formed with a radius of less than 50 nm. When integrated with a gate electrode, field enhancement at the tip showed the promise of very high field emission electron currents especially when arrays of >1 million tips per cm@super 2@ could be produced. Even though currents above a milliamp have been achieved, vacuum microelectronic devices have not been adapted into widespread use. The vacuum environment of the device leads to changes in emission performance and premature failure that has limited the acceptance of the devices. Numerous approaches have been explored to improve and maintain the vacuum environment of the devices and enhance the vacuum conductance. In addition, device structures have been proposed that are less sensitive to the vacuum level and less susceptible to failure. An overview of these issues will be provided from a historical perspective.

Magnetic Interfaces and Nanostructures
Room Exhibit Hall B - Session MI-TuP

Poster Session

MI-TuP1 Comparative Studies of Magnetic Phases of the Interfacial Layers for Co/Ge(100) and Co/Ge(111) Films*, **J.S. Tsay,*** National Chung Cheng University, Taiwan*; C.W. Su,* Academia Sinica, Taiwan*; C.H. Hwang,* Tunghai University, Taiwan*; Y.D. Yao,* Academia Sinica, Taiwan

Magnetic phases of the interfacial layers were comparatively investigated for Co/Ge(100) and Co/Ge(111) films thinner than 13 monolayers using surface magneto-optic Kerr effect technique. Co/Ge(100) films show nonferromagnetic behavior up to 12 monolayers at 300 K. After systematic investigations of the magnetic properties upon cryogenic treatments, magnetic phase diagram of the Co/Ge(100) films was established. The boundary between nonferromagnetic and ferromagnetic phases was experimentally determined to be from below 150 K to above 300 K as the cobalt thickness increases from 9 to 14 monolayers. This behavior is consistent with the thickness-dependent scaling law of Curie temperature for a thin film system. As comparing to Co/Ge(111) system, this boundary shifts to higher Co thickness side. Due to the difference of the electronegativities for Co and Ge atoms, Co LMM Auger line shifts to a higher kinetic energy as the Co thickness increases. This gives the spectroscopic evidence of the formation of interfacial compounds. Co/Ge(100) exhibit a diffused 2x1 diffraction pattern within the first monolayer thickness followed by a diffused background for thicker films as observed using low-energy electron diffraction technique. Ordered structure up to several monolayers were observed for Co/Ge(111) films as deposited at 300 K. In additional, the critical exponent @beta@ï? in the power law relationship of magnetization for Co/Ge(100) films is about 0.38 that lies close to the value expected by three-dimensional Heisenberg model, while the critical exponent of Co/Ge(111) is close to the value of two-dimensional XY model. These experimental evidences show that the structure of Co/Ge(100) interfacial layers is in a much disordered state. This causes a three-dimensional stacking of subsequently deposited Co atoms and furthermore the different magnetic transition behavior of Co/Ge(100) and Co/Ge(111) films.

MI-TuP2 Fabrication and Magnetic Property of Co Platelets On Si (111) Surfaces*, M.H. Pan, H. Liu, J.Z. Wang, J.F. Jia, Q.-K. Xue,* The Chinese Academy of Science, China*; **J.L. Li,** S.Y. Qin, C.-K. Shih,* University of Texas at Austin

Self-organized Co platelets with uniform size and shape were fabricated on Si(111)-7x7 surfaces covered with identical Al nanocluster arrays. The Al nanocluster array not only suppresses reaction between Si and Co, but also enables formation of well-defined Co nano-platelets. These platelets appear as equilateral triangles with fixed orientation and two-monolayer "magic" thickness, and the area of individual plates is quantized in N square units of halves of the 7x7 unit cells. Despite their small volume (a few nm3), these magnetic nanoplateles exhibit unusually high blocking temperature (>100 K).

MI-TuP3 Surfactant Effects on the Growth of FePt Nanoparticles: Toward Core-Shell Nanomagnets*, **A.C.S. Samia,** X.-M. Lin, J.A. Schlueter, J.S. Jiang, S.D. Bader,* Argonne National Laboratory

Nanosized magnetic materials offer interesting possibilities to investigate fundamental physics and create new technologies in sensors, biomedicine and data storage applications. Particularly, magnetic alloy nanoparticles have attracted great interest due to their potential in ultra high-density recording media applications. Among the different nanomaterials being developed for this application is the FePt system. The high magnetic anisotropy, good chemical stability and resistance to corrosion of this material make it an ideal candidate for permanent magnet applications. Furthermore, monodispersed FePt nanoparticles can be readily obtained from the simultaneous reduction of platinum acetylacetonate and decomposition of iron pentacarbonyl in the presence of organic ligand stabilizers. To date most synthetic work has focused on the use of oleic acid and oleyl amine as passivating surfactants. Using this surfactant combination, spherical FePt nanoparticles in the size range of 3-10 nm have been reported. As prepared, the magnetic nanoparticles are superparamagnetic and requires an annealing step to transform them to a more stable magnetic state. Here we report the effects of other surfactant systems on the particle size and growth of FePt nanoparticles. We will present the effects of oleic acid and trioctylphosphine oxide (TOPO) surfactants on the particle size, size distribution and shape of FePt nanoparticles. By gaining insights on the role of these surfactants in regulating the growth of FePt nanoparticles we are able to synthesize larger FePt nanoparticles. To overcome the superparamagnetic limitation in ferromagnetic nanoparticles we are also developing novel core-shell exchange-spring nanomagnets, which consist of hard magnetic (CoPt, FePt) and soft magnetic components (Co). Such combination results to the interaction of the two phases by exchange coupling that leads to a high magnetic energy product.

MI-TuP5 Rotational Loss in Exchange Bias Systems and their Modeling*, **K. Steenbeck,** R. Mattheis, M. Diegel,* IPHT Jena, Germany

The rotational loss E in sputtered AF/F systems (AF: IrMn, thickness t = 0 to 13 nm, F: NiFe, CoFe, CoFe/Cu, thickness about 18 nm) is determined in dependence on AF thickness t by torquemetry at high field and at 10 and 300 K. After onset of E at low thickness a huge loss peak occurs at that thickness where exchange bias starts to develop and goes down to a lower and constant value above a critical thickness t@sub c@. Our simulations are based on a statistical distribution of coupling energies and include new aspects not considered up to now. For the first time rotational loss can be calculated in (111) textured films and the complete thickness dependence of E(t) can be described. Below t@sub c@ we consider crystallites with homogeneous AF magnetization, a 3-axial AF anisotropy K and an AF interface net moment which undergoes irreversible switching for critical values j/Kt. This loss disappears for large t. For t above t@sub c@ we include domain walls parallel to the F/AF interface. Our calculations display that the main loss contribution at that thickness is caused by complete AF 60 ° domain walls created in crystallites with 3-axial anisotropy and strong enough coupling (j above 1.5 @sigma@, @sigma@ domain wall energy). Switching processes of partial domain walls in crystallites having their j/@sigma@ in a critical interval contribute only at low level. The modelling allows to derive numerical values for the coupling energy per spin, the AF anisotropy constant K and the AF domain wall energy @sigma@.

MI-TuP6 Nanostructured Zigzag Shaped Magnetic Devices*, **D.P. Pappas,** F.C.S.S. da Silva, W.C. Uhlig, J. Unguris,* NIST

Magnetism in zigzag shaped thin film elements is investigated using scanning electron microscopy with polarization analysis, magneto-transport measurements, and micromagnetic simulations. We find that the angle of magnetization alternates along the length of the element, and is strongly correlated to the corrugated edges. We show that this simple and unique geometry can be used as a natural means of biasing the magnetization relative to the current to form a magnetic field sensor. In this configuration the sensors are primarily sensitive to fields parallel to the applied current. These results can be interpreted in terms of a coherent rotation model of the magnetization. These devices are scalable to nanometer dimensions.

MI-TuP7 Spin Momentum Transfer Induced Dynamics in Magnetic Nanostructures*, **W.H. Rippard,** M.R. Pufall, S. Kaka, T.J. Silva, S.E. Russek,* NIST*; J.A. Katine, M. Carey,* Hitachi Global Storage Technologies

We have directly measured high-frequency precessional dynamics induced by a dc current I injected into patterned nanopillar devices and continuous spin-valve structures through a lithographically defined nanocontact. The induced magnetization dynamics have been studied as a function of current, material, as well as applied field strength H and direction. For in plane applied fields, the excitation frequency is found to linearly decrease with applied current, in qualitative agreement with single domain modeling. The excited frequencies vary between 5 GHz and 40 GHz as a function of applied field and frequencies of excitation can be well-described by the Kittel equation, indicating that the excitations are ones with wavelengths much larger than the contact size. As the angle of the field is varied with respect to the film plane, the dynamics become more complicated. Abrupt shifts in the frequency occur with applied current applied and df/dI can vary strongly with I at a given field. These shifts can be either to an increased or decreased frequency, depending on the field strength and angle. Moreover, the frequency of precession can be multivalued several different, non-harmonically related frequencies being measured at a given field and current with each mode having a linewidth 18,000. Single domain modeling based on an LLG equation modified to contain a spin-torque term captures a number, but not all, of the behaviors we observe.

MI-TuP9 Undercut Nano Contact-hole Fabrication for a Ferromagnetic Vertical Single Electon Transistor and TMR Enhancement in the Coulomb Blockade Regime*, **S. Haraichi**, T. Wada,* National Institute of Advanced Industrial Science and Technology, Japan

Recently, we have fabricated ferromagnetic single electron transistor s (FSET) with nanometer sized vertical magnetic tunnel junctions and observe d a strong TMR enhancement in the Coulomb blockade regime at relatively high temperature. The FSET consists of under layer drain electrodes, interlayer insulating layer with nano contact-holes, and over layer source electrodes, which is fabricated on an SOI substrate whose cap silicon layer acts as the gate electrode. The key issue of the process is the fabrication of undercut nano contact-holes. We use the bilayer SiO@sub 2@ of high-temperature sputte r layer and low-temperature sputter layer as an interlayer insulating layer. By using the etching rate dependence on sputtering temperature of SiO@sub 2@ in the electron beam direct lithography process, undercut nano contact-hol es have been successfully fabricated with a minimum diameter of 17 nm. Final ly, we have fabricated a vertical crossbar type FSET and obtained over 100% TMR enhancement at 15 K. This TMR enhancement can be modulated by the gate voltage.

MI-TuP10 Giant Magneto Resistance (GMR) Effect in Nanoscale Alternating Magnetic/ Non-Magnetic Metallic Multilayer*, **K.B. Ravi**,* Birla Institute of Technology, India

Giant magneto resistance (GMR) effect in nanoscale alternating magnetic/ non-magnetic metallic multilayers has evinced tremendous interest worldwide. Cu/Co Multilayers have been electrolytically deposited directly on to n-Si substrate from single bath, there by eliminating the need of a conducting seed layer. Magneto resistance is very sensitive to the growth conditions and can be destroyed by intermixing magnetic and non-magnetic interfaces and also by poor crystalline quality of the layers. Co and Cu are weakly miscible elements and for the reason they are most likely to yield chemically sharp interfaces. The observed MR value is Â»1%. Interface characteristics are analyzed using TEM, AFM and EPMA. Aim of the present work is to improve the magneto resistance value in these films by optimizing the deposition conditions and the layer thickness. The studies are going on to find out the effect of Cu layer thickness [by fixing Co layer to 2 nm thick] on MR and also to correlate the interface structure with giant magneto resistance.

MI-TuP11 Interface Chemistry and Structural Properties of Expitaxial Ultrathin Fe Films on MgO(100)*, **E.D. Lu**, V.K. Lazarov, H.T. Johnson-Steigelman, M. Gajdardziska-Josifovska, P.F. Lyman,* University of Wisconsin at Milwaukee

Epitaxial ultra thin Fe films have been grown successfully on MgO(100)(1x1) at room temperature (RT). The chemistry and structures of the interface during Fe film growth has been investigated by low energy electron diffraction (LEED), x-ray photoelectron spectroscopy (XPS). Prior to Fe deposition, commercial MgO(100) substrates were annealed at 750 °C in either furnace in air or ultra high vacuum (UHV) annealing in order to get well-ordered (1x1) reconstruction. We have found that band offsets toward valence band maximum (VBM) for MgO is 2.6 ± 0.2eV at Fe deposition of 5.0 monolayer (ML). We have also identified chemical states present on the initial stage of Fe deposition with elemental Fe@super 0@, Fe@super 2+@, and Fe@super 3+@ species. After deposition of more than 5.0 ML Fe, the elemental Fe becomes dominant, and finally body-centered cubic (bcc) Fe (100) films can be grown epitaxially on MgO(100)(1x1). Upon annealing for improving quality of the epitaxial Fe films, we have found there is an interdiffusion occurring between the Fe films and the MgO(100) substrates and becoming severe upon annealing to 500 °C.

Manufacturing Science and Technology
Room Exhibit Hall B - Session MS-TuP
Poster Session

MS-TuP1 Reactive Preclean H@sub 2@/He Plasma Prior Copper Deposition, Investigation on the First Wafer Effect and Multivariable Advanced Process Control*, **R. Petri**, L. Bucelle,* STMicroelectronics, France

As a general concern in the semiconductor industry, the process stability is crucial and the methodology to ensure this stability becomes more and more complex. By years, the submicron technology constrains the manufacturing to introduce thorough process controls: initially guaranteed by specification limits only, it was improved by the introduction of control limits and Statistical Process Control. Recently, the industry is moving to Advanced Process Control based on a multivariable control of machine parameters. By this way, those parameters can eventually be correlated with product yield. On another hand, process integration becomes extremely sensitive to the process environment and therefore any uncontrolled modification of the reactor surface, such as reactor wall state, wall temperature, in-situ plasma clean, could generate a process drift and may induce severe yield lost or reliability issues. As a consequence, the study and the eradication of the first wafer effect, due to its impact on the manufacturing performances, has generated a lot of focus and publications. This paper is an application of the Advanced Control Process to ensure the stability of the reactive H@sub 2@/He plasma preclean process used in dual damascene structure prior copper deposition. It shows that tiny variations of the wafer processing context are easily detected by appropriate APC model. It appears that plasma potential is very dependant on process controlled parameters but also varies significantly with substrat nature as well as reactor wall temperature. We show that any process drift from the standard expected behavior is detected with the developed model. The nature of the deviation (i.e. signature) is also given. Therefore, in a manufacturing environment, APC is an extremely versatile methodology which can detect in line process drift, but also allows more fundamental investigations, like first wafer effect understanding and eradication, much easier, faster and cost effective.

MS-TuP2 A New Way to Get Steady Trichlorosilane (TCS) Vapor Flow for EPI Deposition Process*, A. Sidhwa, **Z. Lu**, S. Bansal,* STMicroelectronics, Inc*; C. Cross,* STMicroelectronics, Inc.

TCS has been used for many years as silicon source in high temperature EPI applications. It is still preferred in many applications since its low material cost and high deposition rate. In TCS EPI process, hydrogen (H2) is frequently used as carrier gas to convert TCS from liquid to vapor and carry TCS vapor to reaction chambers. The flow of TCS vapor is normally controlled by a Liquid Vapor Controller (LVC). It requires stable TCS liquid temperature to achieve good repeatability of TCS vapor flow. If both low and high TCS vapor flows are required, two LVCs have to be installed in parallel to achieve both low and high flow controls. A traditional LVC controls TCS vapor flow by measuring the mass difference between incoming gas (H2) and outgoing (H2+TCS) of the controller. It can provide steady TCS vapor flow if the temperature of TCS liquid is stable. Since TCS vapor pressure is extremely sensitive to TCS temperature, LVC can no longer provide steady TCS flows if TCS temperature fluctuates. The reason is that the temperature of outgoing gas (H2+TCS) and TCS partial pressure fluctuate according to the fluctuating TCS liquid temperature. In order to resolve the overhead/delay of TCS minibubbler/ conducting lines and their temperatures, a Piezocon flow controller was introduced and installed downstream of the TCS minibubbler. Since Piezocon controller calculates the accurate TCS flows in real time and its located downstream of the whole minibubbler unit, it becomes independent of the TCS liquid temperature. Piezocon controller also has high accuracy and repeatability in a wide range of vapor flows, which includes our low and high TCS applications. Once it combines with a digital MFC, which also has high repeatability in both low and high flow, the combination would provide us very steady TCS vapor flows in both low and high ranges.

MS-TuP3 The Evaluation of a Twin Wire Arc Spray (TWAS) Process for Coated Shields used in Soft-Sputter Etch Pre-Clean Chambers*, **A. Sidhwa**, M. Goulding, M. Kalaga, X. Breurec, R. Pierce, T. Gandy,* STMicroelectronics, Inc

A Soft Sputter Etch (SSE) process plays a vital role in the cleaning of contacts and vias prior to the deposition of contact barriers and via liners. This paper describes the work performed at STMicroelectronics to eliminate Silicon Oxide (SiO2) defects, which are observed at the end of the Pre-Clean chamber component (quartz and shield) lifetime; the latter is specified in RF hours. During the component re-cycling process, the aluminum (Al) RF shield receives a particular surface finish after the cleaning step. It is well known that the Bead-Blast/Post-Blast Etch (PBE) process produces a relatively rough surface finish, which enhances the oxide sticking properties during subsequent wafer sputter-etch. However during such processing, a large surface area of roughness (containing a small number of nucleation sites) is produced on the surface of the shield, resulting in defects (Silicon Oxide flakes) being observed at the end of the Pre-Clean chamber lifetime: i.e., the sputter-etched oxide becomes clustered around a comparatively small surface area, with continuous growth in a vertical direction producing "Worm" defects. The latter defects constitute "stress risers," which are a key source of oxide de-fragmentation. Hence, when trying to increase the sputter-etch chamber component lifetimes from the current 60 RF hours to a significantly higher value of 250 RF hours, the problem of Worm defects becomes more significant. However by contrast, an Al RF shield with a TWAS surface finish shows no similar issues at comparable lifetime. This paper describes the evaluation and implementation of TWAS for the Al RF shield, and explains the significant impact/elimination of Worm defects due to the change in the RF shield surface condition.

MS-TuP4 Two Gas Reactive Sputtering of Oxynitride Compounds: Model and Practice*, **D.C. Carter**, D.J. Christie, W.D. Sproul,* Advanced Energy Industries, Inc.

Reactive sputtering process control has been the subject of much research in recent years. The result of this work has been the development of methods for improving the economy and utility of this popular deposition method. Adding to the understanding of reactive sputtering techniques are functional models developed to explain the dynamics of these often difficult to control processes. Most common, both in practical use and in laboratory research have been deposition processes involving a single reactive gas producing simple binary compounds. Only in the past few years have models been extended to consider the effects of a second reactive gas. Similarly, practical understanding from empirical studies involving two reactive gasses is quite limited. The general rule recognized from models and laboratory experience holds that for the deposition of most compounds effective control in the transition region between the metallic condition and the poisoned condition requires some form of active, partial pressure or similar control. Adding a second reactive gas to the process adds great complexity to the control challenge. Carlsson et al.@super 1@ demonstrated that a two reactive gas process can exhibit a behavior called "trapping" where the sputtering target becomes trapped in a poisoned state. Only through the removal of both reactive gases would the model allow the target to recover from the poisoned state. Based on this the partial pressure of both reactive gases must be controlled to prevent the trapping behavior. We apply such control to a two reactive gas sputtering process, first in deriving solutions to mathematical models and then in practice. Using active, multi-gas control we demonstrate stable two gas reactive sputtering for the oxynitride systems of Silicon, Titanium and Aluminum and within the stable operating space we show film composition control allowing user specified film properties and performance. @FootnoteText@ 1. J. Vac. Sci. Technol., A 11(4), (1993).

MS-TuP5 Hard Mask Dual Damascene Integration Scheme for 65nm*, **G.A. Delgadino**, T.P. Pender, M. Le, S. Li, L.Q. Xia, Y. Ye,* Applied Materials, Inc.

Smaller geometries and the use of lower Îº dielectrics in BEOL integration at 65nm and beyond will require extensive changes in dual damascene integration scheme. Traditional via-first approach reaches its limits as 248nm photoresist is replaced by thinner, weaker, poisoning-prone 193nm photoresist. In this paper presents the development of a hard mask integration solution for extending the implementation of copper/low-Îº interconnect structures at 65nm node and beyond. The scheme overcomes major challenges in low-Îº integration, minimizing ashing damage to low-Îº material and avoiding photoresist poisoning issues associated with 193nm resist. Two Hard mask materials, TiN and W were investigated and potential problems addressed. For the etching point of view, both materials showed good performance but TiN required more tradeoffs due to its lower sputtering resistance and more chemically reactive nature. On the other hand, TiN transparency in part of the visible spectrum, facilitate integration while W required modifications during deposition and/or limitations on the mask thickness. Preliminary Low shear-force CMP with different slurries demonstrated good removal rates for both materials. From the perspective of feasibility and cost, hard mask Dual Damascene appears to be a promising candidate for competitive Copper/Low k integration.

MS-TuP6 Integration of an Ultra Low-k Dielectric in a 300mm 130nm Trench First Dual Damascene Etch Process*, **R. McGowan**, P.J. Wolf,* International Sematech*; D. Wang,* Tokyo Electron America, Inc.

This paper describes a two level metal, 130nm dual damascene etch process development, using an ultra low-k (ULK) dielectric material (k=2.2) on 300mm wafers. The process used a dual hardmask approach in a "Trench First" etch scheme with an interlayer etch stop. Each step requires good uniformity and selectivity to the underlying layers. A BARC etch DOE (used in all recipes) and correct selection of the hardmask & barrier etch chemistries were key factors in the successful etch development. Three iterations, in an overall cycle of improvement, are given as examples, used to take the process from an initial low yield to a robust high yielding process.

MS-TuP7 Effect of Double Polishing Pad on the Shallow Trench Isolation¬Chemical Mechanical Polishing (STI-CMP) Process*, Y.J. Seo, **S.W. Park**,* DAEBUL University, South Korea*; W.S. Lee,* Chosun University, South Korea*; S.Y. Kim,* Dongbu-Anam Semiconductor Co. Inc., South Korea

Chemical mechanical polishing (CMP) technology for global planarization of multi-level inter-connection structure has been widely studied for the next generation devices. CMP process is carrying out by pressing a rotating wafer against a moving polishing pad on which suitable slurry is dispensed. Among the consumable for CMP process, especially, polishing pad set and itâ?Ts material properties play a very important role into the removal rates and global planarization ability of CMP process. In this paper, we investigated the effects of different sets of polishing pad to apply the direct shallow trench isolation (STI)-CMP process using high selectivity slurry (HSS). As our preliminary experimental results, IC1000/JR111 pad set and IC1000/subaIV pad set have the highest selectivity. Even if selectivity is high, because IC1000/SubaIV set shows the low removal rate, we could conclude that IC1000/JR111 set is more superior than IC1000/SubaIV set. Also, the wafer map of hard pad set showed the center-fast type, and soft pad set showed the edge-fast type. Through the above results, we could select the optimum polishing pad set to achieve the direct STI-CMP process without reverse moat etch step, so we could expect the improvements of throughput, yield and stability in the ULSI fabrication process.

MS-TuP8 Effects of Slurry Temperature on the Oxide-CMP Performance*, W.S. Lee, **T.W. Kim**,* Chosun University, South Korea*; Y.J. Seo,* DAEBUL University, South Korea

The mechanical polishing pad and chemical slurry play an important role in chemical mechanical polishing (CMP) which has recently been recognized as the most effective method to achieve global planarization in ultra large scale integrated circuit multi-level interconnections. In this paper, we have investigated CMP performance of SiO2 as a function of different temperature of slurry and pad surface. There are two ways to study the temperature effect on CMP performance: (1) by controlling the temperature of both the pad and slurry at a desired value, or (2) by adjusting only the slurry temperature and keeping the polishing pad temperature. Moreover, the relationship between the removal rate (RR) and zeta-potential as a function of slurry temperature were investigated. According to the preliminary experimental results, it appears that the observed slurry temperature dependence of RR is mainly due to the change of pad surface mechanical property with the slurry temperature. Therefore, the understanding of these temperature effects provides a foundation to optimize an oxide CMP process for ULSI multi-level interconnection technology. This work was supported by a Korea Research Foundation grant (KRF-2002-005-D00011).

MS-TuP9 Impact of Reconditioned PVD Shielding on Process Yield*, D.J. Zuck, **G.H. Leggett**, D.S. Zuck,* QuantumClean

Process control is impacted by many variables in the chamber of a semiconductor process tool. Process chambers often have shielding that is removable and can be reprocessed for reuse. The effective reprocessing of this shielding can have a dramatic impact on process performance. The process deposition must be removed completely and additional contaminates can not be added to the shielding. The shielding is in close proximity to the wafer surface and often can transfer contaminates to the wafer. This shielding can include clamp rings which can contact the wafer in the edge ring exclusion area. The surface condition of this shielding must be maintained. The typical cleaning methodology for the removal of metal deposits from stainless steel shielding is corrosive and can attack the underlying base metal. Changes in surface morphology and finish can result in shorter lifetimes for parts and also have an impact on process yield. Particle contamination can result from shielding that does not have the proper surface morphology and/or surface preparation. A methodology was developed to monitor the surface condition and recondition the part when this surface morphology has deteriorated to a point where it has an impact on process yield. A method was further developed that reconditioned the surfaces and improved the lifetime of these parts. Data will be presented on the mobile ionic contamination of the parts as well as the surface finish and its impact on process performance. A comparison of surface finish with process performance will be described.

MS-TuP10 Silicon Isotope Enrichment by IRMPD of Si@sub 2@F@sub 6@: A Method for High-Efficiency Enrichment of @super 28@Si by Two-Color CO@sub 2@ Laser Irradiation, ***H. Ohba***, *A. Yokoyama, M. Hashimoto, K. Katsumata, H. Akagi,* Japan Atomic Energy Research Institute, Japan*; S. Arai,* Hill Research Corporation, Japan

The natural abundance of silicon isotopes is 92.2% @super 28@Si, 4.7% @super 29@Si and 3.1% @super 30@Si. It has been reported that an isotopically pure @super 28@Si single crystal has a thermal conductivity about 60% higher than that of a natural silicon single crystal at room temperature. This pure material is expected to contribute to the creation of higher-density silicon integrated circuits. Laser isotope enrichment processes promise low energy inputs, low capital costs and lower tails assays, hence significant economic advantages. The infrared multiple photon dissociation (IRMPD) of Si@sub 2@F@sub 6@ leads to the formation of SiF@sub 4@ and SiF@sub 2@. The Si@sub 2@F@sub 6@ with enriched @super 28@Si can be obtained by dissociating the Si@sub 2@F@sub 6@ containing @super 29@Si and @super 30@Si selectively. In order to obtain highly enriched @super 28@Si products in the case of a conventional one-color CO@sub 2@ laser irradiation, however, a high fluence and a large number of laser shot are required, and it is unsuitable for large-scale separation. So, we have studied a rapid and highly efficient method for enrichment of silicon isotopes utilizing isotopically selective IRMPD of Si@sub 2@F@sub 6@ by a two-color laser irradiation scheme. We demonstrated that the dissociation rate of Si@sub 2@F@sub 6@ molecule per pulse increased about 10 times compared with the conventional one-color irradiation. And consequently we were able to acquire the highly enriched @super 28@Si at about one tenth of the laser shots required in the case of the conventional method.

MS-TuP11 Silicon Isotope Enrichment by IRMPD of Si@sub 2@F@sub 6@: Development of Continuous Silicon Isotope Enrichment Technique for Large-Scale Production, ***K. Katsumata***, *H. Ohba,* Japan Atomic Energy Research Institute, Japan*; H. Akagi, A. Yokoyama,* Japan Atomic Energy Research Institute*; S. Arai,* Hill Research Corporation, Japan

Since it had been reported that an isotopically pure @super 28@Si single crystal has high thermal conductivity, it has been growing interests in its use to the high thermal conductive semiconductor substrate. For the expansion of the market of the enriched silicon, it may be necessary to develop a large-scale silicon isotope enrichment method. We have demonstrated a highly efficient silicon isotope enrichment utilizing infrared multiphoton dissociation (IRMPD) of Si@sub 2@F@sub 6@ irradiated with two-color CO@sub 2@ laser@footnote 1@. The scheme consists of two successive steps: At first, the Si@sub 2@F@sub 6@ molecules containing @super 29@Si and @super 30@Si are excited selectively by the irradiation at nearly resonant wavelength with weak pulsed laser beam. Then, the excited molecules are dissociated by the irradiation at non-resonant wavelength with relatively high intense pulsed laser beam. In this report, we developed continuous silicon isotope enrichment technique for the large-scale production, based on this method. An apparatus for continuous isotope enrichment consists of two TEA-CO@sub 2@ lasers, a reaction cell with a gas flow system, and instruments for the monitoring of the abundance of Si in Si@sub 2@F@sub 6@ and the production rate. Si@sub 2@F@sub 6@ gas and buffer Ar gas flowed through a reaction cell with controlling pressure and flow rate. Then isotopically selective IRMPD of Si@sub 2@F@sub 6@ molecules containing @super 29@Si and @super 30@Si were done in the reaction cell by the simultaneous irradiation with two laser pulses at different wavelengths. All of the reaction products were corrected in a trap at 77 K. After the conditions for continuous isotope enrichment had been optimized, @super 28@Si enriched up to 99 % was produced at a rate of 0.7 g/h with the yield of 63 %. @FootnoteText@ @footnote 1@A. Yokoyama, et al., US patent 2003-0034243 A1 (2002).

MS-TuP12 Field Emission Enhanced Semiconductor Thermoelectric Cooler, ***B.L. Weiss***, *P.H. Cutler, N.M. Miskovsky,* The Pennsylvania State University*; M. Chung,* University of Ulsan, South Korea*; N. Kumar,* UHV Technologies

We report the initial experimental results of the fabrication and measurements of a prototype field emission enhanced thermoelectric cooler device. The device is designed for applications in microelectronics, and operating from ambient to cryogenic temperatures. The device is fabricated using CVD deposited wide band gap (diamond and III-V nitrides) thin films. Cooling measurements are carried out in a UHV system using both thermocouple and optical thermometry. This work is motivated by a recent theoretical analysis of an efficient, compact, low power consumption thermoelectric cooler by Chung et. al. @footnote 1@. The new paradigm involves cooling via electron field emission from wide band gap materials which is based on a corrected theory@footnote 2@ of the Nottingham effect @footnote 3@ with calculated cooling rates of up to 100 W/cm@super 2@ or better. The thermoelectric cooler device proposed here uses an electric field modulated current to transport energy (i.e., heat) from a cold source to a hot source via n- and p-type carriers. This device is fabricated by combining the standard n- and p-channel solid-state thermoelectric cooler with a two-element vacuum field emission device inserted into each of the two channels which introduces an essentially infinite thermal resistance for lattice heat conduction. In the proposed cooler, the heat removed from the cold source is the average energy difference of the field emitted electrons from the n-type and p-type semiconductors. The theory predicts the average energy removed (cooling rate) increases with decreasing doping concentration and with increasing local field at the emitter surface. With typical values of doping and field, the cooling rates exceed those of standard thermoelectric coolers. The cooling device is shown to have an energy transport (i.e., heat) per electron of up to 500 meV depending on concentration and field while, in good thermoelectric coolers, it is about 50-60 meV at room temperature.} $Footnotes {@footnote 1@ Moon Chung, P.H. Cutler, N.M. Miskovsky, Nalin Kumar and V. Patel,Solid-State Electronics, 47 1745-1751, 2003. @footnote 2@ Moon Chung, P.H. Cutler, N.M. Miskovsky and T.E. Sullivan,J Vac Sci Technol B;12(2),727-36, 1994. @footnote 3@ W.B. Nottingham Phys. Rev, 59, 907, 1941.

Nanometer-scale Science and Technology
Room Exhibit Hall B - Session NS-TuP
Poster Session

NS-TuP1 Electrostatic Potential and Charge Domain Mapping of Samples by a Large Range Scanning Probe Microscope., ***Y.D. Park***, Seoul National University, South Korea, Korea*; J. Lee, S. Lee, Y.S. Cho, H. Shin, Y. Kuk,* Seoul National University, South Korea

A large range scanning probe microscope was constructed, with a new beam reflection structure. Z scanner was separated from X-Y scanner for fast scanning of massive samples. A high precision (~100 nm) X-Y stepper was used to scan samples over a large area. Double reflection mirrors are used to avoid z positional errors caused by laser beam path. The nanowires and carbon nanotubes are imaged without any distortion on electrode-patterned Si wafer. The scanning range can be varied from tens of nanometer to tens of micrometer with this microscope. The electrostatic potential mapping over many nanowires and the surface charge domain of ferroelectric samples will be given for examples.

NS-TuP2 Fabrication of High Performance NSOM Probe For Optical Trapping, *S.S. Choi, D.W. Kim, C.K. Chun,* ***M.S. Song***, SunMoon University, Korea*; M.J. Park,* Korean Military Academy, Korea

There have been tremendous interests about the optical trapping of the biomolecule in the microdevice with optical spectroscopic capablities. For microdevice application purposes, the optical trapping with nearfield optical probe array seems quite promising. Though, the weak nearfield intensity has been major obstacle for its application. The nearfield optical intensity through the nanosize aperture is dependent upon the aperture size, the grain size of the deposited metallic film, and other factors influencing the surface plasmon excitation. The surface plasmon excitation can be accomplished with periodic texturing of the metal surface around the nanoszie aperture. The enhancement of the nearfield optical intensity can be utilized for the nearfield optical trapping. In this report, the two adjacent metal aperture was fabricated using microfabrication technique including stress-dependent oxidation, isotropic wet etching of silicon oxide and bulk etching of Si, and bimetallic metal deposition. The adjacent nanosize metal aperture with distance less than the input wavelength can improve the output optical intensity. The bimetallic deposition of Ti/Al layer has been performed in order to provide better uniformity of the coated metal film. The buffer layer of Ti thin film would reduce grain size during the reflow process. The reduced grain size of the deposited thin film is supposed to improve throughput of nearfield optical intensity. The fabricated probe array will be utilized for near field optical trapping of the biomolecule. The optical characterization of the fabricated nearfield probe array will be investigated and the biomolecule trapping be tested.

NS-TuP3 Visualization of Two-Dimensional Doping Profile in Si for the Fabrication of Resistive AFM Probe*, **H. Shin**, B. Lee,* Kookmin University, Korea

In recent, scanning resistive probe microscopy (SRPM)@footnote 1@, as a variant of SPM-based techniques, which has a semiconductor resistor at the apex of the tip and can observe surface charges directly, was newly proposed and demonstrated. Spatial resolution of SRPM is dependent upon the size of the prepared resistor at the apex. The size of the resistor can be determined by width of the SiO2 implant mask, where both sides of the mask were open and implanted with As+ ions, and the diffusion length of the ions underneath. Using Kelvin Force Microscopy (KFM), we investigated the area of the resistor or equivalently underneath of the mask and determined the diffusion length of implanted As+ ions. For the first time, the depletion regions in the graded junction between implanted n+ and p-type Si substrate were observed. Furthermore, we proposed the mechanism of the SRPM by the observation of the overlapping depletion regions in the narrow resistor, which results the lowering barrier height for charge carriers. @FootnoteText@ @footnote 1@ H. Park, J. Jung, D.-K. Min, S. Kim, S. Hong, and H. Shin, Scanning Resistive Probe Microscopy: Imaging Ferroelectric Domains, Appl. Phys. Lett., 84, 1734-1736 (2004).

NS-TuP4 Nanoscale Current Mapping of Indium Zinc Oxide Thin Films Investigated by Conducting Atomic Force Microscopy*, **C.Y. Su**,* National Science Council, Taiwan*; H.C. Pan,* National Science Council, Taiwan, Taiwan, ROC*; M.H. Shiao,* National Science Council, Taiwan*; C.N. Hsiao,* National Science Council, Taiwan, R.O.C.

Transparent conducting oxide (TCO) films such as impurity-doped indium oxide systems have been widely applied for opto-electronic devices. Recently, several advantages of ZnO doped indium oxide (IZO) thin film has been reported. Since the photon emissive layer thickness of a device is typically in the range around 100 nm, understanding of the microscopic evidences for improving device performance is required. We have used the technique of conducting atomic force microscopy (CAFM) to investigate the relations between local surface electrical properties and morphologies of IZO thin films treated by different cleaning methods. The conducting regions are attributed to zinc oxide distributed randomly in the average size of 35 nm. Microscopic current mapping indicates ultraviolet-ozone (UV-ozone) treatment is contributed to produce nonconductive region due to generation of stable oxide as reported previously. By applying a tip bias of over -9 V on the nonconducting region, UV-ozone treated sample showed resistance against decomposition while the others failed. This stable oxide acts as a hole transport layer between the photon emissive layer and IZO thin film, which improves stability of devices by decreasing degradation rate of device performance. The surface oxide layer is generally attributed to increasing the work function after UV-ozone treatment, and higher efficiency is achieved as a result of reduction in energy barrier by improving interfacial conditions. Similarly, an additional ultra-thin SiO@sub 2@ layer deposited over IZO thin film would optimize electrical properties for improvement of device performance.

NS-TuP5 A Combined Vapor and Electrochemical Deposition Approach to the Controlled Growth of Nanoscale Metal Dendritic Islands, Beaded Wires, and Continuous Wires*, **C.E. Cross**, J.C. Hemminger, R.M. Penner,* University of California Irvine

Under conditions of careful control of the experimental parameters of substrate temperature and metal atom flux, conventional vapor deposition can be used to grow a variety of useful metal nanostructures. We use this approach to grow dendritic islands as well as beaded nanowires of gold on graphite substrates. Combining this approach with electrochemical deposition allows us to convert beaded nanowires into continuous nanowires (diameters as small as 20nm) that are many microns in length. Low flux vapor deposition of sub-monolayer amounts of gold on a graphite substrate that is held at or near room temperature generates dendritic islands of gold. The islands are fairly monodispersed in lateral dimensions (~100nm across). If the graphite substrate is held at higher temperature (@>=@300°C) "beaded wires" can be grown by decorating the graphite steps. The "beaded wires" are composed of gold "dots" that are 10-20nm diameter. Once again the "beaded wires" consist of gold dots that are highly monodispersed. The "beaded wires" provide excellent nuclei for electrochemical growth of very narrow, long, continuous wires of gold on graphite, where the wires are several microns in length. Each of these classes of structures have potentially interesting uses. The dendritic islands of gold are of interest in studies of the catalytic properties of gold nanostructures. The theoretically expected one dimensional electronic structure and optical properties of linear chains of gold dots that are tens of nanometers in diameter spaced by 10nm are of interest and the long nanometer scale continuous wires of gold are under development for sensor applications.

NS-TuP6 Electrochemically Grown Single Nanowires for Gas and Biochemical Detection*, **C. Lee**, M. Yun, R.P. Vasquez,* Jet Propulsion Laboratory (JPL)*; N.V. Myung,* University of California at Riverside*; E. Menke, R.M. Penner,* University of California at Irvine

We have developed an electrochemical nanowire growth technique which allows the use of a wide variety of sensing materials such as metals, alloys, metal oxides, semiconductors, and conducting polymers. Using this technique, we have grown single 3 micron long Pd nanowires with a diameter of 75 nm. We have also grown single polypyrrole nanowires of 500 nm diameter. The Pd nanowires grown by this technique have been used to sense hydrogen gas and the polypyrrole nanowires have been used as a pH sensor. The Pd nanowire hydrogen sensor operates under ultra low power (~ 25 nW) conditions and exhibits a fast response (<300 ms) due to the small sensor volume. Our hydrogen sensors can detect hydrogen over a wide range of concentrations from 0.02 % hydrogen gas to 10 % hydronge gas and can be used for monitoring explosive concentrations of hydrogen gas. In the case of single nanowire pH sensor, the current change observed upon the change in the conductivity of polypyrrole is 2 nA when 1 microliter of buffered solution at pH 12.45 is placed on top of the single polypyrrole nanowire sensor.

NS-TuP7 Phase Transformation of Copper Oxide Nanowires*, H.-Y. Chen,* National Tsing Hua University, Taiwan*; S. Han,* National Taichung Institute of Technology, Taiwan*; **Y.-B. Chu**,* National Chung Hsing University, Taiwan*; H.C. Shih,* National Tsing Hua University, Taiwan

The phase transformation of Cu@sub 2@O to CuO nanowires has been investigated by x-ray diffraction, transmission electron microscopy, and field emission electron microscopy. The Cu nanowires were firstly electrodeposited into anodic aluminum oxide templates with the pore size of 100 nm. After that, the specimens were annealed in air at 250°C to 900°C. The Cu completely transformed into Cu@sub 2@O above 250°C, meanwhile the CuO phase appeared above 350°C. The CuO phase increased with temperatures, whereas Cu@sub 2@O decreased significantly with annealing temperature increasing. Additionally, the Cu@sub 2@O phase completely transformed into CuO while the specimen annealed at 900°C. The phase transformation is accounted for the changes of Gibbs free energy with temperatures, and the consideration of thermodynamics is further discussed.

NS-TuP8 Polyaniline Nanofiber Chemical Sensors*, **S. Virji**, J. Huang, R.B. Kaner,* University of California, Los Angeles*; B.H. Weiller,* The Aerospace Corporation

Using a new interfacial polymerization method for the synthesis of conducting polyaniline nanofibers, we have developed nanofiber sensors and compared them to conventional polyaniline sensors. Polyaniline nanofiber films give high sensitivity and fast time responses due to their large surface area that allow for easy diffusion of gases into and out of the film. Conventional polyaniline thin films, chemically synthesized by oxidative polymerization and cast from organic solvents, exhibit strong but relatively slow, diffusion-controlled, doping characteristics when exposed to acid or base. In addition to doping and dedoping, polyaniline can also be reduced in the presence of a reducing gas such as hydrazine and swelling effects occur in the presence of organic solvents. This latter process can involve vapor-induced chain alignment of polyaniline in the presence of small alcohols. With a large range of detection capabilities, high sensitivity and time response, polyaniline nanofibers are a promising sensor material.

NS-TuP9 Growth of CNT and Tungsten Nanowires Deposited in HFCVD System*, **M. Passacantando**, L. Lozzi, R. Rastelli, S. Santucci,* University of L'Aquila, Italy

Oplay an important role in testing and understanding fundamental physical concepts, for example, the role of dimensionality and size in optical, electrical, and magnetic properties, but also hold considerable technological promise for new nanodevices applications. Furthermore the growth of these nanostructured materials directly on silicon, silicon oxide and other thin films now used in the microlectronics production process opens new possibilities for a quick application as nanodevices. Multiwalled carbon nanotubes and tungsten nanowires have been directly deposited in a hot filament chemical vapour deposition (HFCVD) system using acetylen (C@sub 2@H@sub 2@) on 3 nm of Nickel film deposited on Pt-Si@sub 3@N@sub 4@ patterned substrate. The CNT have been grown only on Si@sub 3@N@sub 4@ site, with a presence of tungsten wires on the Pt pattern. The as-synthesized products were characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM) and X-ray Photoelectron Spectroscopy (XPS) techniques. The tungsten wires, after the extraction from the deposition apparatus showed a partially oxidised status (WO@sub x@, x=1-2), smooth surface with no amorphous sheath, and a sharp-tip end with diameters in the range of 10-100 nm. The proposed growth method can be easily scaled up for the real applications.

NS-TuP10 Numerical Simulation of Nanostructure Growth*, H.H. Hwang,* NASA Ames Research Center*; D. Bose,* Ames Center for Nanotechnology*; T.R. Govindan, M. Meyyappan,* NASA Ames Research Center

Nanoscale structures, such as nanowires and carbon nanotubes (CNTs), are often grown in gaseous or plasma environments. Successful growth of these structures is defined by achieving a specified crystallanity or chirality, size or diameter, alignment, etc., which in turn depend on gas mixture ratios, pressure, flow rate, substrate temperature, and other operating conditions. To date, there has not been a rigorous growth model that addresses the specific concerns of crystalline nanowire growth, while demonstrating the correct trends of the processing conditions on growth rates. Most crystal growth models are based on the Burton, Cabrera, and Frank (BCF) method, where adatoms are incorporated into a growing crystal at surface steps or spirals. When the supersaturation of the vapor is high, islands nucleate to form steps, and these steps subsequently spread (grow). The overall bulk growth rate is determined by solving for the evolving motion of the steps. Our approach is to use a phase field model to simulate the growth of finite sized nanowire crystals, linking the free energy equation with the diffusion equation of the adatoms. The phase field method solves for an order parameter that defines the evolving steps in a concentration field. This eliminates the need for explicit front tracking/location, or complicated shadowing routines, both of which can be computationally expensive, particularly in higher dimensions. We will present results demonstrating the effect of process conditions, such as substrate temperature, vapor supersaturation, etc. on the evolving morphologies and overall growth rates of the nanostructures.

NS-TuP11 Metal Catalyzed Carbon Nanotube Synthesis by Chemical Vapor Deposition: A First Principles Study of CNT Nucleation and Growth*, **S.H. Lee**, G.S. Hwang,* The University of Texas at Austin

Carbon nanotubes (CNTs) have numerous potential applications ranging from chemical and biological sensors to future electronic devices. Their shape, atomic configuration, and chemical composition could be tailored by tuning process parameters such as temperature and feed gas composition. Such atomic scale control is essential for the development of viable novel chemical, biological and electronic devices. However, still very little is known about underlying growth mechanisms, due largely to a difficulty in direct measurement of complex physical and chemical phenomena occurring during actual CVD processing. While current experimental techniques are still limited to providing complementary real space information, the interplay between experiment and theory will contribute to uncovering complex CNT growth mechanisms and subsequently achieving precise control of their physical and chemical properties. Using density functional theory calculations, we have investigated the initial stage of Ni-catalyzed CNT growth with a feed gas of C2H2/NH3. In this talk, we will present i) decomposition of C2H2 and NH3 which is a strong function of the surface facet of catalysts, ii) hydrogen etching of carbon, iii) diffusion dynamics of decomposed carbon atoms, and iv) formation mechanisms of ring structures from small hydrocarbon species. We will also discuss when the atomic configuration of CNTs will be determined, such as zigzag and armchair structures.

NS-TuP12 Evolution of Single-wall Carbon Nanotubes under Atomic and Molecular Deuterium Treatments*, **E.G. Keim**,* University of Twente, MESA+ Institute, The Netherlands*; W. Lisowski,* Polish Academy of Sciences, Poland*; A.H.J. Van den Berg, M.A. Smithers,* University of Twente, MESA+ Institute, The Netherlands

Relatively little experimental activity has been devoted to the interaction of atomic hydrogen with single-walled carbon nanotubes (SWNTs). Here we present SEM, TEM and XPS data dealing with the question of how the SWNTs are affected by prolonged interaction with a gas mixture of atomic (D) and molecular deuterium (D@sub 2@) at various temperatures. The material, HiPco, was first dispersed in isopropanol in an ultrasonic bath and was subsequently deposited on Si(100). Both the heating of SWNTs and their interaction with deuterium were performed in situ in a quartz cell, part of a separate UHV glass system@footnote 1@, and maintained at 78 or 273 K. The SWNT samples were exposed to the gas mixture, produced by the thermal dissociation of D@sub 2@ on a hot W filament, its temperature, T@sub f@, being kept at 1020 and 1550 K for a deuterium pressure of 0.005 and 0.5 Torr, respectively. All gas-solid interactions were monitored in situ by Thermal Desorption Mass Spectrometry (TDMS). See Ref.@footnote 2@ for a description. The spectroscopic and microscopic examinations were performed ex situ. Prolonged interaction of the (D + D@sub 2@) gas mixture produced at T@sub f@ = 1020 K leads to a coalescence of bundles of SWNTs forming large diameter carbon ropes of square and triangular cross-section covered by nano-aggregates of graphite material. Both the coalescence of single SWNTs and a massive reconstruction of bundles of SWNTs into multi-walled nanotubes were found to occur after prolonged exposure of the SWNTs to the gas mixture produced at T@sub f@ = 1550 K. Similar evolution phenomena were observed earlier@footnote 3@, however, after annealing the SWNTs under Ar flow above 2000 K. @FootnoteText@ @footnote 1@ W. Lisowski, Vacuum 53, 13 (1999).,@footnote 2@ W. Lisowski, E.G. Keim and M.A. Smithers, J. Vac. Sci. Technol. A21, 545 (2003).,@footnote 3@ K. Méténier, S. Bonnamy, F. Béguin, C. Journet, P. Bernier, M. Lamy de La Chapelle, O. Chauvet, S. Lefrant, Carbon 40, 1765 (2002).

NS-TuP15 Theoretical and Experimental Studies on the Adsorption of Oxidizing Gas on Carbon Nanotubes Thin Films*, **L. Lozzi**,* University of L'Aquila, Italy*; L. Valentini,* University of Perugia, Italy*; S. Picozzi, C. Cantalini, S. Santucci,* University of L'Aquila, Italy

In this work a combined theoretical and experimental study on CNT-based system for gas sensing applications is reported. Carbon nanotubes thin films have been deposited by chemical vapor deposition on Si3N4/Si substrates provided with Pt electrodes. Microstructural features as determined by SEM, TEM and Raman spectroscopy highlight the growth of defective tubular carbon structures. The electrical resistivity of the CNT film shows a temperature dependence semiconducting-like and a p-type response with decreasing electrical resistance upon exposure to NO2 gas and O3. No response has been found by exposing the film to CO gas, while some other concomitan gases may have an interfering behavior [1]. In order to obtain a theoretical validation of the experimental results, the equilibrium position, charge transfer and density of states are calculated from first principles for the CNT+CO and CNT+NO2 and CNT+O3 systems. Our density functional calculations show that Both CO and NO2 and O3 molecules adsorb weakly on a defect free tube wall, with essentially no charge transfer between the tube and the molecules. The electronic properties of CNTs are sensitive to the adsorption of NO2 and O3 due to an acceptor-like peak close to the tube valence band maximum, while they are insensitive to the CO adsorption. According to the experimental findings, our theoretical results suggest that gas-induced modification of the density of states close to the Fermi level might significantly affect the transport properties of nanotubes. The role of the defects on the wall of CNT is also discussed and related to the experimental results. In particular the anomalous adsorption of O3 that produces a consumption of the CNT film also at low temperatures is explained as the effect of the chemisorption of this gas onto defective sites. [1] C.Cantalini, L.Valentini, I.Armentano, L.Lozzi, J.M.Kenny and S.Santucci. Sensors and Actuators B 95, 195 (2003).

NS-TuP16 Oxygen Functionalized MWNT as Active Layer for Gas Sensing: Detection of NO@sub 2@ and NH@sub 3@*, A. Felten,* LISE, Belgium*; R. Ionescu, E. Sotter, E. Llobet, X. Vilanova, X. Correig,* Universitat Rovira i Virgili, Spain*; C. Bittencourt, **J.-J. Pireaux**,* LISE, Belgium

Due to their large surface area, Carbon Nanotubes (CNTs) show the potential to be applied as the active material of gas sensors. However, the presence of a thick graphite-like layer at the surface of the nanotubes can rule out the sensing potentiality of this material. In this work we use inductive RF oxygen plasma to functionalize the surface of nanotubes. The influence of different plasma conditions (power, treatment time and pressure) on the functionalization of the CNT surface was studied by XPS. The analyses showed that when a too high power is applied, a chemical etching occurs at the surface and the metallic precursors used in the CNT syntheseis are exposed. On the other hand, for an optimized range of the parameters, functional groups (hydroxide, carbonyl, carboxyl) are attached to the CNT while a reduction in the amount of graphite at the CNT surface is observed. After characterization, functionalized MWNTs (Nanocyl Â®) were used to form the sensitive layer of micro-hotplate gas sensors, prepared by the drop coating method. Detection of NO@sub 2@ and NH@sub 3@ concentrations as low as 500 ppb and 200 ppm, respectively, was found to be possible at ambient temperature. Plasma treatment showed to improve the sensing potentiality of CNTs by reducing the thickness of the graphite-like layer at their surface. The presence of the residual metallic catalysts at the CNTs surface proved to play an important role in sensitivity.

**NS-TuP17 Synthesis and Property of Carbon Nanosheets at Different Deposition Temperatures*, M.Y. Zhu*, *J.J. Wang, X. Zhao, R.A. Outlaw, D.M. Manos, B.C. Holloway,* College of William and Mary

Carbon nanosheets, a novel form of free-standing graphite sheets with thickness less than 1 nanometer, were synthesized by radio-frequency (13.56MHz) plasma enhanced chemical vapor deposition (PECVD) on Silicon, quartz and tungsten foil. Carbon source, methane (CH@sub 4@), was diluted in hydrogen (H@sub 2@) to produce carbon nanosheets at various temperatures 650°C to 900°C. SEM images show that the surface morphology of carbon nanosheets varies a lot with deposition temperature. Lower deposition temperatures produce large, smooth nanosheets while higher temperatures produce small, corrugated nanosheets. Raman spectroscopy indicates that the crystallinity of nanosheets deteriorates with increasing substrate temperature. Diode I-V curves were acquired to study the field emission property of nanosheets grown at different temperatures, and yield a turn on field of as low as 4 V/µm.

NS-TuP18 Modeling, Fabrication and Characterization of Vertically Aligned Carbon Nanofiber (VACNF) Based Triode Field Emission Devices for Use in Massively Parallel Digital E-Beam Array Lithography (DEAL)*, X. Yang*, University of Tennessee at Knoxville*; W.L. Gardner, L.R. Baylor, H. Cui, D.K. Hensley, R.J. Kasica, D.K. Thomas,* Oak Ridge National Laboratory*; M.A. Guillorn,* Cornell Nanofabrication Facility*; M.L. Simpson,* Oak Ridge National Laboratory

Field emission triodes have been fabricated for application in massively parallel Digital E-beam Array Lithography (DEAL) at Oak Ridge National Laboratory (ORNL)@footnote 1@. Vertically Aligned Carbon Nanofibers (VACNFs) were individually grown as the field emission cathode elements. Three electrodes are fabricated: the cathode, the extraction electrode and the focus electrode, separated from each other by 1µm SiO@sub 2@. We have demonstrated Fowler-Nordheim emission characteristics and electron beam focusing. The variation of beam diameter with focus aperture potential observed both optically and lithographically agrees well with electron beam simulations. Further modeling indicates that these devices will benefit from thicker (500 nm vs. 100 nm) electrodes in three ways: (1) improved focus effectiveness; (2) decreased optimal-beam size; and (3) increased depth of focus. The capability to realize thicker electrodes using a low-pressure chemical vapor deposition (LPCVD) tool is being implemented based on these results. Effects on beam shape and size due to electrode or field emitter offsets from coaxial geometry were also investigated with a 3D structure simulation. It was shown that a converged electron beam shape of 50nm or less in diameter is still obtained in the presence of small geometrical offsets. Preliminary 3x3 arrays of these devices have been fabricated and are being tested. While the extraction and focus electrodes are individually addressed the cathode is presently common to all devices. Individually addressed cathode designs, important for implementing DEAL with dose control circuits integrated into the device, are being investigated. Details of device modeling, fabrication, and characterization as well as device development to minimize offsets and realize individual cathode addressing will be presented. @FootnoteText@ @footnote 1@ ORNL is managed by UT-Battelle, LLC, for the U.S. Department of Energy under contract No. DE-AC05-00OR22725.

NS-TuP19 Microstructure Modeling of MOCVD Zirconium Oxide Deposition*, M.O. Bloomfield*, Rensselaer Polytechnic Institute*; Z. Song, B.R. Rogers,* Vanderbilt University*; T.S. Cale,* Rensselaer Polytechnic Institute

We use PLENTE, a software designed to study the formation and evolution of microstructure in thin films, to evaluate different models of growth for high vacuum MOCVD of zirconium oxide films on a selection of substrates. ZrO2 is a potentially important high-k dielectric material that can be deposited using zirconium tertbutoxide (ZTB). Cross sectional TEM and AFM of films in the early stages of growth show different wetting and island formation behavior as a function of deposition conditions, substrate selection, and history. Using PLENTE, TEM data and XRD data, we develop models of how islands grow during deposition and compare the evolving structures with experiment, primarily through trajectories of instantaneous void fraction measured experimentally via in situ spectroscopic ellipsometry. Models that include highly wetting islands and strong lateral growth show distinctly different voiding behavior from those with preferential growth non-parallel to the substrate, and in some cases, can be directly mapped to observed growth trajectories. Finally, we use the models developed to predict grain structural development for deposition onto rough and featured substrates, as demonstrations of possible use for integration of ZrO2 films into more complicated microelectronic structures.

NS-TuP20 Fabrication and Characterization of Carbon Nano-Cone Electron Emitters*, K. He*, *N. Badi, A. Bensaoula,* University of Houston

R&D on effective field emitter arrays (FEAs) is now concentrated on nano-structured solid materials because of the significant local increase of the electric field on solid tips with a small radius of curvature. This paper reports on the electron field emission behavior from uncoated and boron nitride coated graphite nano-cones. Since nano-cones emit most of their current into a single narrow beam, it is expected that graphite nano-cones electron emitters will lead to a significant improvement in the performance of high-resolution electron-beam instruments as well as for high power microwave amplifiers. Fresh cleaved highly oriented pyrolytic graphite (HOPG) was surface treated with poly-l-lysine for adhesion purpose. By dipping the sample into a colloidal gold solution with particles with a nominal diameter in the range of 30-50 nm, naturally and uniformly dispersed gold nanoparticles are attached to the HOPG surface. These nanoparticles serve as a mask for a subsequent reactive ion etching process to form the graphite nano-cones. Higher etching rates under oxygen plasma were observed at a plasma power above 180 Watts. Depending on the oxygen plasma etching parameters such as power and etching time, nano-cones with different shapes and sizes were fabricated. A sulfur doped boron nitride coating was deposited on the etched HOPG nano-cones using an ion assisted physical vapor deposition technique. Field emission characteristics from different coated and uncoated HOPG nano-cones will be presented along with their thermal and temporal stability measurements under different pressure environments. Acknowledgment: This material is based upon work supported by the National Science Foundation under Grant No. 0010100 and by NASA cooperative agreement to TcSAM. The authors would like to thank Dr. N. Medelci for his valuable help.

NS-TuP21 Epitaxial Growth of Nisi@sub 2@ on (001)Si Inside 50-200 Nm Openings Prepared by Scanning Probe Lithography*, S.-Y. Chen*, *S.D. Tzeng, S. Gwo,* National Tsing Hua University, Taiwan*; L.J. Chen,* National Tsing Hua University, Taiwan, Republic of China

Epitaxial growth of NiSi@sub2@ on (001)Si inside Si@sub3@N@sub4@ openings of 50-200 nm in size prepared by AFM tip-induced local oxidation has been investigated. From TEM and SEM observation, the size of the openings was found to influence significantly on the morphology of epitaxial NiSi@sub2@. As the dimension of the openings decreases, the shape transition of facetted NiSi@sub2@ from irregular polygons to inverse pyramids was found inside openings. NiSi@sub2@ facetted rods would appear as the size of the openings was further decreased. The results are attributed to the increased interface/volume ratio of silicides with decreasing size of openings and the non-uniform stress distribution within the miniature openings. As the thickness of Ni and annealing time are well-controlled, it is possible to obtain the identical NiSi2 pyramids of nano-scale even though the shape of openings is not identical.

NS-TuP22 Nanoscale Patterning by Pulsed Laser Irradiation and Nanoparticle Alignment*, Y.F. Guan*, *A.J. Pedraza,* The University of Tennessee, Knoxville

One- and two-dimensional nanostructure arrays have been generated in silicon by pulsed-laser irradiation, using a Lloyd's mirror configuration. The nanostructures consisted of periodic ripples and protrusions that could reach an amplitude of 20 nm and a height of 80 nm, respectively. The ripple nanostructure was used as a template for the alignment of gold nanoparticles. The gold was first sputter-deposited on the rippled surface at a grazing angle, and subsequently annealed at 700 °C. Atomic force and high resolution scanning electron microscopy studies revealed that the nanoprotrusions are preceded by the formation of extended ripples. The present experiments show that the Lloyd's mirror configuration strongly enhances the formation of ripples and that nanoprotrusions form at the intersection of two mutually orthogonal sets of ripples. On the other hand, when a Lloyd's mirror is not added only 1-D ripple formation was observed, with no protrusions. Interference of the incoming or refracted laser beam and the laser light scattered by the surface undulations has been long recognized as the cause of periodic ripple formation. It is concluded that the gradient of surface tension arising from a temperature gradient is responsible for the formation of the nanoripple structure, and the breakdown of the ripples into aligned nanoprotrusions is due to a second temperature modulation along the ripple lines. The intersection of two mutually perpendicular ripple structures and the very high reflectivity of the nanoprotrusion tips are the causes that promote this secondary laser light modulation.

NS-TuP23 Electronic and Ionic Processes in Local Oxidation of Titanium Nitride Thin Films*, **N. Farkas**, J.R. Comer, G. Zhang, E.A. Evans, R.D. Ramsier,* The University of Akron*; J.A. Dagata,* National Institute of Standards and Technology

We report an apparently unique property of titanium and titanium nitride thin films to undergo local oxidation or vaporization during scanning probe microscope (SPM)-based lithography. Nanometer-scale oxide dots or holes can be produced reliably depending on reversible SPM tip preparation. The presence of an electron-blocking tip oxide results in oxide growth on the substrate, while its absence leads to electronic breakdown. Both tip conditions can be obtained in a sequential and reversible manner. Electron emission is investigated using a variety of metallic and semiconducting SPM tips. Changing the nitrogen content of the deposition plasma over a wide range alters structural and electrical properties of the substrate materials and provides a basis for understanding the underlying processes, which we characterize by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), SPM roughness, and four-point probe measurements. This work contributes to a better understanding of the electronic and ionic components of the total current during SPM-assisted oxidation and demonstrates that this technique can be used to both modify and to characterize materials on the nanometer scale.

NS-TuP24 Synthesis and Characterization of Germanium Nanocrystals*, **H. Gerung**,* University of New Mexico*; S.D. Bunge, T.J. Boyle,* Sandia National Laboratories*; C.J. Brinker, J. Lee, M. Osinski, S.M. Han,* University of New Mexico

Semiconductor nanocrystals promise numerous potential applications, ranging from phosphors to biosensors. Herein, we focus on synthesis and characterization of Ge nanocrystals (NCs). Compared to group III-V or II-VI compound semiconductor NCs, the synthesis of Ge NCs in solution has been a challenge due to their covalent bond nature. Very few solution-phase syntheses have been reported, and the precursor preparation often involves a relatively high-pressure (>1 atm) process. We have developed a new method of synthesizing Ge NCs. The size of these crystals ranges from 3 to 10 nm. The control over shape and size dispersion of Ge NCs will be discussed in this presentation. We will present the effect of processing temperature and precursor concentration on the size. The synthesis relies on solution reduction of Ge@super 2+@ to Ge@super 0@ with commercially available precursors at relatively low temperature (300 °C) and at 1 atm of Ar ambient. This new synthetic route is scalable for mass production of Ge NCs. Photoluminescence spectra of Ge NCs show emission from 380 to 510 nm, and they demonstrate the quantum confinement effect of Ge NCs. However, ultraviolet-visible (UV-Vis) spectroscopy and attenuated-total-reflection Fourier transform infrared spectroscopy (ATR-FTIRS) show that Ge NCs are sensitive to air exposure, and they degrade over time in the absence of proper surface passivation. We therefore utilize different types of surfactants to encapsulate and stabilize the Ge NCs. The stabilized Ge NCs can be then incorporated into a silica matrix via sol-gel approach to form a self-assembled 3-dimensionally (3-D) ordered matrix.

NS-TuP25 Fabrication of SiGe Nanodot Array by Anodic Aluminum Oxide Templation*, **W.J. Huang**,* National Nano Devices Laboratories, Taiwan*; F.M. Pan, D.M. Chen,* National Chiao Tung University, Taiwan

Anodic aluminum oxide (AAO) has a highly ordered hexagonal pore array structure, and has been widely used as a template for nanostructured materials fabrication, such as carbon nanotubes and TiO@sub 2@ nanodots. Silicon germanium (SiGe) is an interesting semiconductor, which has a higher carrier mobility as compared with silicon, and has tunable bandgaps depending on the atomic composition of Ge. Moreover, SiGe is process-compatible with existing Si IC technologies. In conjunction with the AAO templation method and simple dry etching, we have prepared SiGe nanodot array with a dot size smaller than 50 nm. Si@sub 0.85@Ge@sub 0.15@ 50 nm in thickness was deposited on the Si wafer by ultrahigh vacuum chemical vapor deposition (UHV-CVD), followed by the sputter-deposition of TiN (20 nm). An Al film 4 µm in thickness was thermally evaporated on the TiN surface for the AAO preparation. The Al film was anodically oxidized in an oxalic acid electrolyte at room temperature, and the finished AAO pore array has a pore diameter about 60 nm. As the Al layer was completely oxidized, the underlying TiN layer was partially oxidized as well resulting in the formation of the TiO@sub 2@ nanostructure array with a pattern in compliance with the AAO pattern. The TiO@sub 2@ array was then used as the hardmask for dry-etching the remaining TiN and the SiGe bottom layer, and the SiGe nanodot array was thereby produced. Various analytical techniques, such as TEM, AFM and AES, have been employed to characterize the process steps of the SiGe nanodot array.

NS-TuP26 Site-selectivity of Chemical Reaction on a Biomimetic Super-hydrophobic/Super-hydrophilic Micropatterned Template*, **N. Saito**, Y. Wu, M. Kouno, Y. Inoue, O. Takai,* Nagoya University, Japan

Recently, the materials fabrication based on biomimetics attract the attention of many researchers due to their green process, high function and novel self-organized structure. In nature, there are super water-repellent plant leaves such as lotus and taro. These surfaces are covered with hydrophobic micropapilla. The presence of hydrophilic group on such a structure leads to ultra water-repellency. Water droplets would be formed on only super-hydrophilic regions when water was spilled over an artificial super-hydrophobic/super-hydrophilic micropattern on substrates. In this study, we focused on the fabrication and application of biomimetic super-hydrophobic/super-hydrophilic micro-pattern using the microwave plasma-enhanced chemical vapor deposition (MPECVD) and vacuum ultra violet (VUV) lithography. Silicon wafer was used as substrates. Raw materials in the MPECVD were trimethylmethoxysilane (TMMOS) and Ar. The super-hydrophobic/super-hydrophilic pattern was fabricated by VUV irradiation thorough a TEM mesh. In order to confirm the pattern, surface water droplet was observed by environmental SEM. We successfully demonstrated site-selective electroless Cu plating on the pattern from the FE-SEM images.

NS-TuP27 Mechanical Property and Nano Texture of Alumina-Silica Ultra Water Repellent Films*, **M. Bekke**, Y. Wu, N. Saito, M. Koga, Y. Inoue, O. Takai,* Nagoya University, Japan

Ultra water repellent (UWR) films have attracted significant attention due to both fundamental scientific interests and practical applications. It has been known that UWR film requires the surface with two factor, that is, adequate surface roughness and low surface energy. Wenzel and Cassie found a rule between surface roughness and water repellency. The surface roughness can be obtained using various fabrication methods such as sol-gel, plasma enhanced chemical vapor deposition (PECVD) and spray coating. Mechanical property of the film with large roughness is generally inferior to that of the smooth surface film. This is a crucial problem for an industrial application of UWR film. Therefore, it is necessary to improve the mechanical property of UWR film. In this research, we aim to prepare a UWR film with favorable mechanical properties using microwave plasma enhanced chemical vapor deposition (MPECVD). UWR film was fabricated on Si (100) substrate using the microwave plasma-enhanced chemical vapor deposition (MPECVD). Raw materials were trimethylmethoxysilane (TMMOS), CO@sub 2@ and Aluminum(III) diisoproxide ethylacetoacetate(ADE). The flux of the bubbling gas(CO@sub 2@) was changed and the quantity of the ADE was adjusted. The water-repellency of film was evaluated by water contact angle measurements. The surface morphology of UWR film was acquired by atomic force microscopy (AFM) and field emission scanning electron microscopy (FE-SEM). The chemical bonding states were characterized by Fourier transform infrared spectroscopy (FT-IR) and X-ray photoelectron spectroscopy (XPS). The mechanical properties of the film were evaluated by nanoindentation test.

NS-TuP28 Behavior of Water Microdroplets on Nano-textured Surfaces Fabricated by a Focused Ion Beam Technique*, **M. Kouno**,* Nagoya University, Japan*; Y. Wu, N. Saito, M. Koga, Y. Inoue, O. Takai,* Nagoya University, Japan

Water repellency emerged on hydrophobic surfaces has attracted much attention due to fundamental and scientific interests. Surface nano-texture is a key factor for water repellency. Water repellency is generally evaluated by water contact angle. The water contact is usually evaluated in macrometer-scale. Environmental scanning electron microscopy (E-SEM) has the potential of the evaluation in micro-meter scale. In this study, we investigated the correlation between the surface structure and the water repellency based on the observation of water droplets in micro-scale using E-SEM. We prepared two types of samples with different nano-textured surface fabricated by a focused ion beam (FIB) technique. One was consisted of a fine array of concave structures with the center distances being 1 µm on Si(100) substrate. The other was composed of a similar array of convex structures. Their diameters were varied from 150 to 800 nm. All the sample surfaces were modified with the formation of a self-assembled monolayer from heptadecafuluoro-1,1,2,2-tetrahydro-decyl-1-trimethoxysilane [a type of fuloroalkylsilane, FAS, F@sub 3@C(CF@sub 2@)@sub 7@(CH@sub 2@)@sub 2@Si(OCH@sub 3@)@sub 3@] through chemical vapor deposition. These samples were observed by ESEM (Nikon, ESEM-2700). Water droplets were in situ formed on each sample surface by cooling the sample down to ca. 2.5 @super o@C, which is lower than the dew point under the condition of observation chamber. E-SEM images of the water droplets revealed that the water repellency of the sample depends on the shape and the array pattern on the surface in nanometer-scale.

NS-TuP29 Formation of Nanometer-scale Gap Electrodes Based on a Plasma Ashing Technique*, Y. Lee,* Sungkyunkwan University, Korea*; **Y. Roh**,* Sungkyunkwan University, Korea, Republic of Korea*; K.-S. Kim,* Sungkyunkwan University, Korea

Realization of nano- and/or bio-electronic devices requires the formation of metal electrodes with a nanometer-scale gap. Recently the fabrications of metal electrodes 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, special techniques such as electromigration-induced break junction, shadow deposition, or electrochemical deposition have to carry out in order to reduce further the nanometer-scale gap between two metal electrodes formed by microlithography as above-mentioned. One of the proposed techniques to overcome a resolution limit of an optical lithography was a photoresist (PR) ashing technique, in which the minimum linewidth can be formed by ashing the PR pattern defined by the optical lithography. In this work, we proposed a noble and reproducible method to fabricate nanometer-scale gaps between two metal electrodes using PR ashing and lift-off techniques. Using this technique, we obtained metallic electrodes with a nano-gap of less than 10 nm. With this technique, the gaps between two electrodes could be easily controlled and reproduced.

NS-TuP30 Fabrication of MOS Structure with NiSi@sub 2@ Nanocrystals Embedded in Silicon Dioxide*, **P.-H. Yeh**, C.H. Yu,* National Tsing Hua University, Taiwan*; L.J. Chen,* National Tsing Hua University, Taiwan, Republic of China*; H.H. Wu, T.-C. Chang,* National Sun Yat-Sen University, Taiwan*; P.T. Liu,* National Nano Device Laboratory, Taiwan

A metal-oxide-semiconductor (MOS) structure with NiSi@sub 2@ nanocrystals embedded in the SiO@sub 2@ layer has been fabricated. From the TEM micrograph and diffraction pattern, the nanocrystals were identified to be NiSi@sub 2@. The mean size and the aerial density of the NiSi@sub 2@ nanocrstals were estimated to be ~ 7.6 nm and 3.3 x 10@super 11@/cm@super 2@, respectively. A pronounced capacitance-voltage hysteresis is observed with a memory window of 1 V under the 2-V programming voltage. The process of the structure is compatible with the current manufacturing technology of semiconductor industry. The structure represents a viable candidate for low-power sub-100 nm nonvolatile memory devices.

NS-TuP31 The Formation of Au-nanowires Using DNA Molecule as a Template*, **H.-J. Kim**, Y. Lee, I.-S. Yi,* Sungkyunkwan University, Korea*; Y. Roh,* Sungkyunkwan University, Korea, Republic of Korea*; B. Hong, H.-G. Jee, S.-B. Lee, M.-J. Shin, S.-G. Kim,* Sungkyunkwan University, Korea

The formation of metal nanowires via the conjugation of biomaterials (e.g., DNA molecules) and metal nanoparticles has been extensively investigated to obtain highly ordered electronic components for nanocircuitry and/or nanodevices. Metal nanowires were organized by the hybridization of nucleic-acid-functionalized metal or metallic nanoparticles with DNA molecule as a template. For example, Au-nanowires (AuNWs) were formed using the DNA molecules conjugated by aniline- and lysine-capped Au nanoparticles (AuNPs). In this work, we developed a simple technique to form Au-nanowires by the conjugation of 4-aminothiolphenol-capped gold nanoparticles (ATP-AuNPs) and the immobilized DNA molecules on 3-Aminopropyltriethoxysilane (APS) coated Si wafers. In this technique, a metallization process involves three steps: (1) DNA molecules were immobilized on the Si/APS substrate, (2) ATP-capped AuNPs were formed via strong chemical reaction between thiol (-SH) group of ATP and AuNPs, and (3) AuNWs were then formed by the interaction between DNA and ATP-AuNPs. In addition, we investigated the effects of the relative molar quantity (i.e., AuNPs/ATP) on the network formation of Au-nanowires. Our preliminary works indicate that the relative molar quantity may decide the structure of Au-nanowires. These results, as well as further interpretation of the data, will be presented at the conference.

NS-TuP32 Photoluminescent Emission Properties of Porous Nanostructured Y@sub 2@o@sub 3@:eu Thin Films*, **P.C.P. Hrudey**, M. Taschuk, Y.Y. Tsui, R. Fedosejevs, M.J. Brett,* University of Alberta, Canada

Nanostructured photoluminescent thin films of europium-doped yttrium oxide (Y@sub 2@O@sub 3@:Eu), a well-known luminescent material, were grown using electron beam evaporation, in combination with the Glancing Angle Deposition (GLAD) technique. GLAD makes use of controlled substrate motion during extremely oblique physical vapour deposition (PVD) of a thin film resulting in a high degree of control over the nanostructure of the film. Films were deposited using pre-doped Y@sub 2@O@sub 3@:Eu source material. Scanning electron microscopy and x-ray diffraction were used to characterize film nanostructure, while the light emission properties of these films were characterized by photoluminescence measurements. In order to improve the photoluminescent response of the films a post-deposition annealing treatment was used. By annealing in air at 850°C, the film crystallinity improves leading to increases in the photoluminescent response by greater than three times that of the as-deposited samples. The emission properties of vertical posts, helices, and normally-incidence solid thin films were obtained and compared. In studying the effect of film structure on the emission properties vertical posts films were found to emit two times more light in the direction normal to the substrate surface than solid films that contained an equivalent mass of material. Additionally, optical filter devices incorporating Y@sub 2@O@sub3@:Eu were fabricated and studied for their effects on the emission properties.

Organic Films and Devices
Room Exhibit Hall B - Session OF-TuP
Poster Session

OF-TuP1 Fabrication of Micro-Pumps for Organic Micro-Fluidic Devises using Asymmetric Electrode Arrays*, **H.G. Jeong**, M. Dhayal,* Dongshin University, South Korea*; H.J. Lee,* Chonnam National University, Korea*; J.S. Choi,* Dongshin University, South Korea

Recently micro-fluidics devises are of a great interest to use in fabrication of "lab-on-a-chip" and micro electromechanical systems (MEMS). A new types of microelectrodes structures have been developed for controlling fluid movement in micro-systems using AC electric fields. In our research we are developing a design tool of asymmetric electrode arrays to fabricate micro-fluidic devises to use in control of different biological fluids. An optimisation of performance of the bio-MEMS fabricated using conventional techniques such as photolithography and reactive ion etching in our study has been also investigated.

OF-TuP2 Investigation on the Interfacial Reaction of Metal/Fluorinated Polymide*, **C.-Y. Yang**, S.L.-C. Hsu, J.-S. Chen,* National Cheng Kung University, Taiwan

In this work, the surface states of fluorinated polyimide synthesized from 6FDA-BisAAF-PPD, before and after plasma treatment, were characterized by X-ray photoelectron spectroscopy (XPS). The interfacial states of metal-fluorinated polyimide were examined by XPS after metal films of Cu, Cr and Au were deposited onto the fresh cured fluorinated polyimide with or without plasma treatment. The influence of plasma treatments on interfacial reaction was examined. XPS analysis results reveal that the surface of fluorinated polyimide will be oxidized and nitridated after O2 and N2 plasma treatment. In the metal/polyimide interface, chemical bonding of Cr-C is observed in the untreated polyimide system. However, no metal-carbon bonding is found in the Cu, Au and polyimide interface. Slight interface change is observed after the N2 plasma treatment. In addition to M(metal)-C bonding, M-C-O bonding is also observed at the metal-polyimide interface in those samples with O2 plasma applied to the polyimide surface. The relationship between adhesion and interfacial reaction of metal/fluorinated polyimide, and the role of fluorine in the interfacial reaction are also discussed.

OF-TuP3 XPS and FTIR Studies of Dye Molecule Doped Conducting Polymer Films*, **H. Kato**, S. Takemura,* Kanto Gakuin University, Japan*; O. Nishikawa, M. Taniguchi,* Kanazawa Institute of Technology, Japan

Conducting polymer polythiophene(PT) films incorporated with dye molecule such as brilliant green(BG) were prepared by electrochemical doping and diffuse injection methods. Charge transfer and interaction between the doped dye molecule and PT polymer chains were investigated by analyzing the core-level energies and spectral profiles of the atomic components. Vibrational states of the doped dye molecule and the polymer backbone were also investigated by FTIR RAS and ATR in order to examine the dopant configuration into polymer chains in the hybrid films. In the case of brilliant green doping, XPS core-level analysis of S 2p split indicates simultaneous doping of BG cation and HSO4- in the hybrid films prepared by electrochemically reduced and dye diffuse injection methods. Synthesized film samples were categorized into two types by the difference of S 2p core-level energy shift. In the cation-like doped sample, the energy shift of the lower peak of S 2p suggests the charge transfer between BG molecule and polymer chains creating a n-type conducting polymer state. The polymeric state and the dopant configuration were also investigated by FTIR. CH in plane modes of the PT backbone which appeared around 750 cm-1 and ring stretching modes which appeared around 1050 cm-1 indicate the polymeric structure based on a thiophene ring. The profile of the vibrational spectra reflected the detailed polymeric structure. The orientation of the dopant BG molecule in the hybrid films was discussed by analyzing the benzene out-of-plane mode of a BG molecule which appeared at 2000 cm-1.Three possible BG configuration models were closely discussed.

OF-TuP4 Effects of High Electric Fields on Charge Transport and Morphology in Solution Processed Conducting Polymer Films, ***P.S. Chung****,* *P.H. Holloway,* University of Florida

One of the attractive qualities for using organic materials for electronic applications is their ability to be processed in solution, which ultimately leads to lower processing costs. A major obstacle preventing organic electronics from obtaining a greater share in todayâ?Ts technological markets is their inferior performance characteristics when compared to traditional inorganic materials. Polymer and molecular orientation are key issues in governing the electrical and morphological properties of the film. In this study, spincoated films consisting of p-type polymers (i.e. polyvinyl carbazole) and n-type dye molecules (i.e. 3,9-perylenedicarboxylic acid dissobutyl ester) are subjected to high electric fields (200 V/cm to 15,000 V/cm) during solvent evaporation. The polar sidegroups and branches on the polymer and molecule adjust their orientation under the electric field, thereby improving the electrical and morphological properties of the film. Models to quantitate these effects will be presented and discussed.

OF-TuP5 Topology and Growth Behavior of Evaporated Organic Films on Crystalline Metal Layers: Perylene-3,4,9,10-Tetracarboxylic Dianhydride (PTCDA)*,* ***K. Seo****,* *M. Haythe, C. Bonner,* Norfolk State University

PTCDA films were prepared on metal films under four different deposition conditions employing all combinations of low and high substrate temperature with various deposition rates. The films were grown by organic molecular beam deposition (OMBD) in an ultrahigh vacuum chamber from a Knudsen cell, using sublimation temperatures of 430, 380 and 330 ºC, respectively. The grazing-incident-angle x-ray diffraction (GIXD) technique has been measured the anisotropy of the structure in the directions perpendicular and parallel to its surface. We have used the real-time in-situ spectroscopic ellipsometry to determine the optical functions of PTCDA films. The influence of the substrate temperature on the metal films is investigated using spectroscopic ellipsometry and atomic force microscopy. We have found that the grain size of the crystallites and surface roughness increase with increase substrate temperature.

OF-TuP6 Poly(3-hexylthiophene) Organic Thin Film Transistor on Polyimide using Electroplated Gold Electrodes*,* ***J.G. Lee****,* *S.H. Cho, S.W. Na, N.-E. Lee,* Sungkyunkwan University, South Korea

Organic thin film transistors (OTFT) on flexible substrate using electroplated gold electrodes have potential advantages in the fabrication of low cost sensors, smart cards, and field-effect transistors. This method can be a competitive candidate for OTFT applications requiring large area coverage, structural flexibility, low temperature processing, and especially low cost. In particular, the application of electroplating enables one to obtain electrode with high aspect-ratio and good reliability in terms of mechanical flexibility and thermal stress. In this work, poly(3-hexylthiophene) (P3HT) OTFT device uses a top gate structure with electroplated Au source and drain electrodes. Organic thin film transistors (OTFTs) were fabricated using (P3HT) as a semiconducting layer and electroplated gold (Au) as source and drain electrodes. 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 investigated by plasma treatment of polyimide substrate by using Au/Cu/Cr/polyimide structures. Cu(seed)/Cr(adhesion) layers were sputter-deposited in sequence on the plasma-treated polyimide substrate. Then, a negative photoresist, SU-8, was spin-coated on the Cu/Cr/polyimide substrate and patterned by ultra-violet photolithography for source and drain electrodes. After photolithography, Au source and drain electrodes were electroplated into the patterned SU-8 mask. After P3HT film was spin-coated, SiO@sub 2@ gate dielectrics and Al electrode were evaporated with a shadow mask. The channel length ranged between 10 and 25 µm, and the channel width was 800 µm. Electrical properties of fabricated OTFT were characterized and the effect of various process conditions and structures on the performances of fabricated devices will be discussed. Keyword Organic thin film transistor, P3HT, Au electroplating, polyimide, flexible devices.

OF-TuP7 Influences of Ion Irradiation for Depositing Aluminum Cathode in Organic Light-emitting Diodes*,* ***S.M. Jeong****,* *W.H. Koo, S.H. Choi, S.J. Jo, H.K. Baik,* Yonsei University, Korea*; S.J. Lee,* Kyungsung University, Korea*; K.M. Song,* Konkuk University, Korea

To demonstrate the effects of argon ion irradiation during cathode deposition, aluminum cathode prepared by ion beam assisted deposition process on spin-coated soluble phenyl-substituted poly-p-phenylene-vinylene (Ph-PPVs) thin films have been investigated and compared to those by thermal evaporation. Although energetic particles of Al assisted by Ar+ ion may damage the organic material, I-V-L characteristics are improved by applying thin Al buffer layer. It may be deduced from the smaller contact resistance between Al and Ph-PPV induced by large contact area, increase of density of state and lithium diffusion in ion beam assisted device. In addition, highly packed structure of Al cathode inhibits the permeation of H@sub 2@O and O@sub 2@ into Ph-PPV film through pinhole defects, and thus retards dark spot growth. In conclusion, the lifetime of organic light-emitting device (OLED) has been extended through ion beam assisted deposition process.

OF-TuP8 The Effect of Atmospheric Pressure Plasma Treatment on Indium Tin Oxide Anode for Organic Electroluminescent Devices*,* ***S.H. Choi****,* *S.M. Jeong, W.H. Koo, H.K. Baik,* Yonsei University, Korea*; S.J. Lee,* Kyung Sung University, Korea*; K.M. Song,* Kon Kuk University, Korea

The effect of atmospheric pressure plasma (APP) treated indium-tin-oxide (ITO) substrate on poly (9,9-dyoctilfluorene) (PFO)-based light-emitting diodes was studied. It was found that the chemical composition and surface roughness at the ITO surface were changed after APP treatment. Organic light-emitting diodes (OLEDs) fabricated on APP treated ITO surfaces showed three times better electroluminescence and current injection than OLEDs fabricated on as-received ITO surfaces, due to the increase of the smooth contact area between the ITO surface and the organic layer. The ITO substrate after APP treatment showed similar behavior of LPOP. Therefore, APP is an effective treatment for enhancing the performance of OLEDs.

OF-TuP9 Characterization of Porphyrin Monolayers Bearing (O, S, and Se) on Si and Au: Towards Hybrid Memory Storage in Electronic Devices*,* ***A.A. Yasseri****,* *F. Zaera,* University of California Riverside*; J.S. Lindsey,* North Carolina State University*; D.F. Bocian,* University of California Riverside

We report on the characterization of a novel group of redox-active porphyrin molecules synthesized with terminal chalcogen subunits for attachment on to electro-active surfaces. A series of porphyrins has been prepared and characterized as surface bound redox-active monolayers. The molecules designated as (ZnPBz-,ZnPCH2-) bear two linker types substituted on a meso-position of the porphyrin and are terminated with a diverse series of surface anchor groups in free and protected form (hydroxy, S-acetylthio, and Se-acetylseleno) for attachment to Si (100) and Au (111). Communication with the covalently bound adsorbates is achieved through activation of pre-patterned Si-hydride test-platforms to anchor the Si-O, Si-S, or Si-Se tethers to the surface. Similar monolayers were prepared as SAMs on Au yielding analogous Au-S and Au-Se tethers for comparison. Each porphyrin was investigated on Au and Si surfaces using X-ray photoelectron spectroscopy, Fourier transform infrared spectroscopy, and various electrochemical methods including (fast scan cyclic voltammetry, swept-waveform AC voltammetry, and open circuit amperometry). The objective of the study was to demonstrate the (1) the chemical robustness of monolayer binding through each anchor group to the surface, (2) measure the packing density of the molecular monolayers on each surface, (3) and to probe the influence that terminal surface anchor groups (O, S, Se) and linker type bear on the electron transfer (in presence of applied potential) and charge retention (in absence of applied potential) characteristics of the monolayers on each platform. XPS, FTIR, and voltammetric measurements confirm semi-quantitative displacement of surface di-hydride species with -O, -S, and -Se terminated porphyrins, respectively. The electron transfer kinetics of the Si-O, Si-S, and Si-Se indicate that the kinetics strongly depend on the linker type and surface concentration of the porphyrin monolayers, independent on the substrate used.

OF-TuP10 Assembly of Synthetic Molecular Motors on Surfaces*, **T. Takami,*** Visionarts Research, Japan*; T. Ye,* The Pennsylvania State University*; J.M. Tour,* Rice University*; K.-I. Sugiura,* Tokyo Metro. Univ., Japan*; P.S. Weiss,* The Pennsylvania State University

We attempt to assemble synthetic molecular motors mounted on Au{111} and graphite surfaces. Two kinds of molecular motors are proposed: (1) in-plane rotation of molecular rotors: the substrate-bound shaft of the rotor assembly, a metal porphyrin is attached to the shaft through axial ligation with a pyridine group, (2) perpendicular rotation of molecular rotors: sandwich porphyrins are used for the tables to stand on the surface and a perpendicular bifunctional shaft is attached between the porphyrins. The rotation of the molecular motors will be imaged with scanning tunneling microscope (STM) in air and in solution, and will be detected via single molecule resonance spectroscopy with alternating current STM (ACSTM).

OF-TuP11 Chemical Conversion Patterns of the 1,7-octadien Monolayer on Si(111) Surface*, **S.H. Lee,*** Nagoya University, Japan*; N. Saito,* Nagoya University, Japan, Japan*; T. Ishizaki, O. Takai,* Nagoya University, Japan

The organic monolayer covalently attached to silicon has been expected to have a better chemical resistivity compared to organosilane monolayer. The Si-C interface provides a good electronic property for molecular devices constructed on silicon substrate. Many researchers have reported the structural configurations and the chemical bonding states of such organic monolayers. However, scanning probe lithography on the organic monolayers has been reported scarcely. In particular, the electronic properties of nanopattern lithography have not yet been understood. In this study, we investigated the surface potential at the locally scanned area, i.e., nanopattern, onto an organic monolayer formed on a Si substrate. An oxide layer on a Si substrate was removed using chemical etching for 15min in NH4F solution. The substrate was immersed in 1,7-octadien (OD) solution heated at 120°C for 1hour. The OD molecules reacted with the hydrogen-terminated Si surface, resulting in the formation of an OD-monolayer on the substrate. Atomic force microscope (AFM) lithography on the OD-monolayers resist was performed using SPI-3800N AFM with a Si probe in contact mode by applying a positive or negative bias. The pattern on the OD-monolayers resist was fabricated by VUV irradiation thorough a mask. The chemical changes of the OD surfaces were traced by Kelvin probe force microscope (KFM), AFM and fluorescence-labeled spheres.

OF-TuP12 Site Specific Binding of Analyte Gases on Metallophthalocyanine Thin Films: Dft Calculations and Sticking Probability Measurements*, **N.L. Tran,*** University of California, San Diego, U.S.A*; G.C. Poon, S. Bishop, A.C. Kummel,* University of California, San Diego

Several groups report the use of metallophthalocyanines (MPcs) as thin film resistive sensors for analyte gases such as NO@sub x@, CO, O@sub 3@ and NH@sub 3@; however, the chemisorption energies and mechanisms for these gases reacting with various MPcs have not been studied. Density functional theory (DFT) calculations performed in this study show that chemisorption energies vary strongly with metal center and analyte. These calculations also investigate the mechanism of chemisorption. Four analyte binding sites on the MPcs were investigated computationally: (i) metal centers, (ii) inner ring nitrogen atoms, (iii) outer ring nitrogen atoms, and (iv) organic rings. For NO@sub 2@ on FePc and CoPc as well as NH@sub 3@ on FePc , the simulations show chemisorption onto the metal centers and physisorption onto the outer ring nitrogens and organic rings. These calculations also show a multi-step absorption mechanism in which NO@sub 2@ initially binds to the inner ring nitrogens and subsequently migrates to the deep chemisorption well on the metal centers for FePc and CoPc. In contrast, only physisorption was observed for any bonding sites of NO@sub 2@ on NiPc and NH@sub 3@ on CoPc and NiPc. Sticking experiments are being performed to investigate the chemisorption mechanism and selectivity.

OF-TuP14 Organic Polymer Thin Films Deposited on Silicon and Copper by PECVD Method and Characterization of Their Electrochemical and Optical Properties*, **I.-S. Bae**, S.-H. Cho, Z.T. Park, J.G. Kim, J.-H. Boo,* SungKyunKwan University, South Korea

Polymer-like thin films have been deposited on glass, silicon and copper substrates at temperature range of room temperature and 100 °C by plasma enhanced chemical vapor deposition (PECVD) method using Cyclohexane as a precursor for analysis their electrochemical and optical characteristics. Cyclohexane was utilized as organic precursor, and hydrogen and Ar were used as a bubbler and carrier gases, respectively. In order to compare the difference of the corrosion resistant and the optical properties of the plasma polymerized organic thin films with conditions of various RF (radio frequency using 13.56 MHz) power in the range of 20~50 W and deposition temperature. The optical and electrical properties of the as-grown plasma polymerized thin films were analyzed by FT-IR, UV-Visible spectroscopy, I-V and C-V curves. The corrosion protective abilities of Cyclohexane were also examined by AC impedance measurements in 3.5 wt.% NaCl solution. We found that the corrosion protection efficiency (P@sub K@), which is one of the important factors for corrosion protection in the interlayer dielectrics of microelectronic devices application, was increased with increasing RF power. The highest P@sub K@) value of plasma polymerized Cyclohexane film was (85.26% at 50 W), AFM and SEM showed that the polymer films with smooth surface and sharp interface could be grown under various deposition conditions.

OF-TuP15 Damage Mechanism of Emitting Polymer Treated by Low Pressure Plasma*, **D.Y. Lee**, H.K. Baik,* Yonsei University, Korea*; K.M. Song,* Konkuk University, Korea*; S.J. Lee,* Kyungsung University, Korea

In this study, we investigated the damage mechanism of emitting polymer (poly(9,9-dioctylfluorene)(PFO)) films for organic light emitting diode (OLED). For top emission organic light emitting diode (TOLED), indium tin oxide (ITO) films are used as a cathode material due to its high transparency in visible light. In conventional, ITO is deposited by RF/DC magnetron sputtering. But there have been many reports that sputtering process including high energy ions and neutrals degrades emitting polymer. Therefore, metal buffer layer must be inserted between emitting polymer and ITO films, not only to improve electron injection but also to prevent polymer damage. It is very important to reduce a thickness of buffer layer as thin as possible so that low driving voltage and high transparency are achieved. However, low thickness of buffer layer is not effective in prevention of polymer damage from magnetron sputtering. So, this problem is pending unsolvable. We used plasma treatment on emitting polymer (PFO) to eluciate damage mechanism so as to find effective solution for polymer degradation. Low pressure glow discharge was perform with He and O2 gas at 2ï,´10-1 torr. Anode electrode is patterned ITO films and hole transport layer is PEDOT. Al/LiF films were deposited on blue Emitting polymer (PFO) as a electron injection layer and cathode buffer. ITO films was fabricated by RF magnetron sputtering at room temperature. ITO target (SnO2: In2O3 = 1: 9) was sputtered by mixture gas of argon and oxygen. Oxygen partial pressure, working pressure and other deposition parameters were optimized. RF coupled DC was used as a power source and its voltage was changed from 45 V(only RF) to 350 V(only DC). The temperature of cesium reservoir was varied from 80 to 200 Â°C. Negative sputtered particles including In, Sn, O and electron were generated from the target surface and accelerated to the substrate by target voltage.

Plasma Science and Technology
Room Exhibit Hall B - Session PS-TuP
Poster Session

PS-TuP1 CVD Chamber Cleaning by F2 Remote Plasma Processing*, **S.C. Kang**, J.Y. Hwang, N.-E. Lee,* Sungkyunkwan University, South Korea*; K.S. Joo, G.H. Bae,* Shihwa Indus. Com, South Korea

Cleaning of chemical vapor deposition (CVD) chamber during the deposition of SiO @sub 2@, Si @sub 3@N@sub 4@, Si, and W thin films in Si device manufacturing fabs has been carried out using perfluorocompounds (PFCs) including C @sub 2@F@sub 6@, NF @sub 3@, C @sub 3@F@sub 8@, and C @sub 4@F@sub 8@ etc. During CVD chamber cleaning using PFCs, effect of re-emitted PFCs on global warming and difficulty of cleaning the silicon oxide layers have been of great concern. F @sub 2@ cleaning is expected to get rid of the global warming effect completely and contribute to a reduction of operating costs by the use of on-site F @sub 2@ generation systems. However, adoption of F @sub 2@ CVD chamber cleaning has been limited due to high toxicity and reactivity of F @sub 2@ gas. In this study, we carried out CVD chamber cleaning experiments by F@sub 2@ remote plasma generated from a toroidal-type remote plasma source in a commercial 8-inch plasma enhanced chemical vapor deposition (PECVD) system. In this experiment, bottled F @sub 2@ gas was used. Due to difficulty of handling F @sub 2@ gas, various safety measures for storage and delivery were made. Chamber cleaning experiments of silicon oxide layers including PE-TEOS and BPSG were carried out by varying the F @sub 2@ /Ar gas flow ratio, flow rate, pressure, and temperature. Species emitted during cleaning were monitored by Fourier transformed infrared spectroscopy (FT-IR) and residual gas analyzer (RGA). Under the current experimental condition, cleaning rate was increased with F @sub 2@ gas flow rate increased. Destruction removal efficiency (DRE) of F @sub 2@ gas was calculated by evaluating the emitted F @sub 2@ gas during cleaning using residual gas analysis. Effect of various process parameters on cleaning process will be discussed in detail.

PS-TuP2 Design and Development of an Advanced Dielectric Etch Tool using Simulation*, **K. Bera**, Y. Ye, D. Hoffman, G.A. Delgadino, J. Carducci,* Applied Materials, Inc.

Creating a successful all-in-one (main etch, PR ash, and clean) chamber for dual damascene etch requires thorough understanding of the relationships among plasma density, ion energy, and distribution of charged and neutral species to achieve operational capability over a wide range of plasma density and ion energy at widely different pressures and gas flows. This paper presents several aspects of hardware design and process optimization for a 300mm etcher for 90nm technology and below in which simulation was used to gain insight into these phenomena. Plasma simulations demonstrated that higher frequencies generated denser plasma for a given power than lower frequencies, which focused the selection of source frequency for the reactor. Higher frequencies were shown to improve the dissociation fraction promoting creation of desirable facet-protecting polymers. Simulations further revealed that higher frequencies produced lower-energy, less potentially damaging ion bombardment to the wafer. Simulations guided effective chamber cleaning using source. Confinement ring design was optimized using plasma simulation that allowed us to confine plasma for clean mode operations. Flow simulation calculated chamber conductance guiding the chamber design for wide process window. Simulation showed that Neutral Species Tuning Unit (NSTU) can tune pressure and velocity uniformities, and hence CD-bias and profile uniformities. Separate control of plasma density and energy distribution from distribution of neutral and charged species within the chamber was used to demonstrate independent optimization of the etch rate and CD-bias uniformities for dual damascene trench etch process.

PS-TuP3 Spectroscopic Study of Effect of Wall Conditions on Gas Phase and Surface Phase Chemistries in Inductively Coupled Fluorocarbon Plasmas*, **B.S. Zhou**, E.A. Joseph, S.P. Sant, L.J. Overzet, M.J. Goeckner,* University of Texas at Dallas

The effect of wall conditions including dimension, material, temperature, and cleanliness on the gas phase and surface phase chemistries in CF@sub 4@ plasma etching of Si was studied in the modified Gaseous Electronics Conference (mGEC) reference cell. In the mGEC, Al inner walls of various diameters were used to confine the plasma to the center of the chamber and induce changes in the gas phase chemistry. The range of the wall temperature was 25 -150°C. The gaseous molecules and radicals monitored included CF@sub 4@, CF@sub 3@, CF@sub 2@, SiF@sub 4@ and COF@sub 2@, among which CF@sub 4@ and SiF@sub 4@ were found to be the two dominant species, accounting for about 80% of the total concentration. The density ratio of SiF@sub 4@ and COF@sub 2@ was about 2:1 with no bias on the substrate and increased to ~6:1 when Si substrate etching took place. Specifically, as the Si etch rate increased, the COF@sub 2@ density dropped, likely due to suppressed etching of the quartz source window, while the density of SiF@sub 4@ increased. These rates are likely linked through the atomic fluorine density. In addition, the CF@sub 3@ radical density was observed to increase over time. This is indicative of increased surface production of fluorocarbon species from CF@sub x@ film on the wall. This work is supported by a grant from NSF/DOE, CTS-0078669.

PS-TuP4 Stabilizing Plasma and RF Generator Interactions*, **V. Brouk**, R. Heckman,* Advanced Energy Industries, Inc.

Current trends towards reduced semiconductor feature sizes has pushed many etch processes into lower pressure regimes, which challenges both stable and accurate RF power delivery at relatively low output power levels. Variations in plasma impedance are more pronounced at lower output powers as compared with operation at higher power levels. In low pressure plasmas that process electronegative gases, operation at low RF output power can result in plasma instabilities that may be attributed to the dynamic interaction between the power-dependent plasma impedance and load-dependent RF delivery system. The power supply and match network control circuits are often unable to counteract these instabilities, sometime even exasperating the problem, resulting in uncontrollable and unrepeatable variations in process parameters. In this study, we will investigate the electrical model that describes how the plasma processing system and the RF delivery system can interact to influence the stability of the plasma. A means for quantifying and measuring the combined stability factor for the RF delivery system and plasma will be shown. This study will review the differences between slow and fast instabilities, and discuss both active and passive stabilization techniques that can increase the stability region for the RF generator and plasma system.

PS-TuP5 Effect of Magnetic Field on the Characteristics of Internal Linear-type Inductively Coupled Plasma Source*, **G.Y. Yeom,*** Sungkyunkwan University, South Korea, Korea*; K.N. Kim, S.J. Jeong,* Sungkyunkwan University, South Korea

Due to the increase of substrate size and the requirement of high rate processing, large-area high density plasma sources are required for both microelectronics and flat panel display industry. 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 source can not be easily applied to the flat panel display processing due to the standing wave effect, increased capacitive coupling, etc. In our study, a large area (1020mm x 830mm) internal linear inductively plasma source was investigated as a possible high density plasma source for the application to flat panel display processing. Especially, in this presentation, the effect of permanent magnet array on the large area (1020mm x 830mm) linear internal inductively coupled plasma source will be discussed. By the various arrangements of the permanent magnet arrays relative to the inductive source, the uniformity of the plasma has changed significantly, and, by optimizing the magnet arrangement, the plasma uniformity of 2% could be obtained on the substrate. Also, with the optimized magnet arrangement, the photoresist etch rates showed about 60% higher etch rates compared to those without the magnetic field in 15mTorr O@sub2@ gas.

PS-TuP6 Mass and Optical Spectroscopic Studies of an Inductively Coupled Oxygen Plasma*, **P.F. Kurunczi**, V.M. Donnelly,* University of Houston

Mass spectrometry and optical emission spectroscopy were used to measure atomic O in a high-density, inductively coupled oxygen plasma. The plasma reactor consists of a water cooled quartz tube surrounded by a coil powered at 13.56 MHz. An electromagnet confines the high density plasma to the center of the chamber. The walls of the plasma chamber are coated with aluminum oxide. The quadrupole mass spectrometer was line of sight with the center of the plasma. The plasma species pass through a 2mm dia. orifice in the wall of the reactor and traverse through two differentially pumped chambers. With the plasma chamber at 10 mTorr we obtain a background pressure of 5 x 10@super -9@ Torr in the mass spectrometer. The resulting molecular beam was chopped at 103 Hz. with a tuning fork placed between the last aperture and the entrance to the ionizer, resulting in a beam to background signal intensity ratio of 30:1. Gated pulse counting in phase with the chopping frequency was used to subtract the background from the beam signal. With the plasma off a strong beam signal was observed at mass 32 and a weak signal at mass 16 due the small amount of dissociative ionization of O@sub 2@ at the mass spectrometer ionization energy of 23 eV. With the plasma on the signal at mass 16 increases dramatically due to the formation of oxygen atoms in the plasma. From the known cross sections of O and O@sub 2@ we computed the absolute O atom densities with the plasma on. O atom densities increase proportionally with power and inversely with pressure, reaching 6.5% of the total density at 500 W and 2 mTorr. At 8mTorr and 500 W the percent O dropped to 2.5%. The inverse pressure dependence is ascribed to an increase in electron temperature and resulting increase in the dissociation rate constant. Optical emission actinometry measurements from the center and in directly in front of the mass spectrometer sampling orifice will also be reported and compared with the mass spectroscopic results. Work supported by the Petroleum Research Fund.

PS-TuP7 Sub Millimeter Absorption Spectroscopy of Oxygen Containing Fluorocarbon Etching Plasmas*, **E.C. Benck**, K. Siegrist,* NIST

The role of oxygen in fluorocarbon etching plasmas is investigated using sub millimeter wavelength absorption spectroscopy. The plasmas were created in a specially modified capacitively coupled Gaseous Electronics Conference (GEC) Reference Reactor with a commercial electrostatic chuck. Photoresist and SiO@sub 2@ blanket coated wafers were etched in C@sub 4@F@sub 8@/O@sub 2@/Ar, C@sub 5@F@sub 8@/O@sub 2@/Ar, and C@sub 4@F@sub 6@/O@sub 2@/Ar discharges. The absolute density of various radicals (CF, CF@sub 2@, CHF@sub 3@, COF@sub 2@, CO, etc.) were measured as a function of the percentage of oxygen in the feed gas mixture using a sub millimeter source based on a 48x frequency multiplication chain. These results are also compared to the oxygen containing fluorocarbon gas C@sub 4@F@sub 8@O.

PS-TuP8 In Situ Diagnostics in a High Density Inductively Coupled Methane Discharge*, **T. Meziani**, P. Colpo,* Joint Research Centre of the European Commission, Italy*; P.R. Ranson,* GREMI - Orleans University, France*; F. Rossi,* Joint Research Centre of the European Commission, Italy

The high plasma density, independent control of the ion energy, and low-pressure operation of the inductively coupled plasma source made it very successful for dry etching processes. However, its wide operating pressure range makes it also a tool of interest for PECVD. In this work, a novel inductively coupled plasma source was used for the chemical vapour deposition of diamondlike carbon coatings from a methane precursor. This source uses a special arrangement where the coil antenna is embedded in a magnetic core thus offering high efficiency, high plasma density and very good uniformity. This paper presents the plasma diagnostic of the methane discharge carried out by means of Langmuir probe, mass spectrometry including ion energy distribution measurements, and optical emission spectroscopy. Langmuir probe measurements could be successfully applied taking care of removing systematically the insulating carbon layer formed on the probe tip. The plasma density, electron temperature, and eedf were measured varying different process parameters like inductive power, total pressure, residence time, and gas mixture. Different features were found with EEDF ranging from Maxwellian to Druyvestein or to a bi-temperature distribution at lower pressures. Coupled with mass spectrometry, the probe measurements allowed for the estimation of the absolute mass-resolved ion fluxes impinging on the substrate. The ion energy distributions (IED) were also determined and gave some insight on the formation of the different ions bombarding the growing carbon layer. Mass spectrometry measurements showed that CH@sub 4@ is almost totally dissociated in this source when working with flow rates around 40 sccm at 20 mtorr. Finally, relative radical concentrations were assessed by mass spectrometry and optical emission spectroscopy. The diagnostics results were correlated to the analysis of the carbon coatings and helped explaining the growing mechanisms in our reactor.

PS-TuP9 Electron Probe Currents in ICPs*, **F.F. Chen**,* UCLA

Measurements of plasma density and electron temperature with Langmuir probes in low-density RF plasmas depend on proper compensation for oscillating potentials, but there are further difficulties. In regimes where Orbital-Motion-Limited (OML) theory should be valid, we find that the electron saturation current (Ie) cannot be obtained; instead, Ie rises almost linearly with probe voltage Vp. By monitoring the floating potential with a second probe, we find that a positive Vp on a cylindrical probe greatly affects the space potential Vs, dragging it up with Vp so that saturation is never obtained. This occurs even in a grounded chamber and is characteristic of all electrodeless discharges. The reason is that a large Ie to the probe has to be balanced by an equal ion current to the walls. To increase this ion current, an ambipolar potential has to be set up to push the ions outward against charge-exchange collisions. The drift in Vs to the new equilibrium state can take from milliseconds to seconds. Thus, a DC measurement gives erroneous results and must be corrected by the change in Vs. Another effect is an enhancement of the ion current at large negative Vp. This is probably due to the effect of ion-neutral collisions on the orbiting. Suggestions for improved probe techniques will be presented.

PS-TuP10 Spatio-temporal Characterization of Pulsed, Electron Beam Generated Plasmas for Materials Processing*, **S.G. Walton**, D. Leonhardt,* Naval Research Laboratory*; C. Muratore,* ASEE Postdoctoral Fellow*; R.F. Fernsler,* Naval Research Laboratory

In plasma-based materials modification, regulating the flux of ion, neutral, and radical species at the substrate surface is a critical component of process control. The plasma density determines the flux while the electron temperature influences the energy of these species and so both can be used to regulate reactive species at the substrate. To this end, both modulated plasma production and remote plasma sources are typically employed to control the relative ion and radical fluxes and energy through temporal or spatial variations in the bulk plasma. In this paper, spatio-temporal characterizations of pulsed, electron beam-generated plasmas produced in molecular gases will be presented. Mass and time-resolved measurements of ion fluxes and energy distributions are presented and correlated to measurements of the plasma density, potential, and electron temperature. Previous work has shown that energetic electron beams are efficient at producing high-density plasmas (n@sube@ > 10@super11@ cm@super-3@) with low electron temperatures (T@sube@ < 0.5 eV) over the volume of the beam. The resulting species fluxes and ion energy distributions at remotely located electrodes have unique characteristics and can be useful in range of processing applications. Namely, low ion energies (< 4 eV), regimes of large atomic-to-molecular ion ratio (>1), and ion-to-radical fluxes that are adjustable with electrode position. Modulating the electron beam can further enhance these attributes. Measurements are presented for a range of operating conditions and electron beam-to-electrode distances for plasmas produced in nitrogen, oxygen, TEOS and mixtures thereof. The results compliment and are used to understand various processing applications under development in our laboratory. This work supported by the Office of Naval Research.

PS-TuP11 Study on Relation Between CF2 Radicals and Plasma Parameters in ICP Plasmas with Laser-Induced Fluorescence and Wave Cutoff Probe*, **J.-H. Kim**, Y.-S. Yoo, Y.-H. Shin, K. Chung,* Korea Research Institute of Standards and Science, Korea

The behavior of CF2 radical was studied in CF4 inductively coupled plasma. CF2 radical was measured using a laser-induced fluorescence method [1,2]. Absolute electron density was measured using a cutoff probe [3], which was newly developed, and the electron temperature was measured using a double probe to study relation between the electron property and CF2 radical. CF2 density is drastically changed by variations of operating pressure, ratio of mixed gases and RF source power. To examine the relation between electron density and CF2 radical, CF2 radical and electron density were measured as varying the RF power which is a major external parameter influencing to the electron density. As the RF power was increased, CF2 radical density increased in the range of low electron density and then decreased over a critical electron density. Dependence of CF2 radical density on the electron density was theoretically analyzed with rate equations. The theoretically analyzed relation between the electron density and the CF2 radical density was in good agreement with the experimental result. @FootnoteText@ [1] G. Cunge, P. Chabert and J.P. Booth, J. Appl. Phys. V89, p7750 (2001). [2] S. Hayashi, K. Kawashima, M. Ozawa, H. Tsuboi, T. Tatsumi, and M. Sekime, Sci. and Tech. Adv. Mat. V2, p555 (2001). [3] J.H.Kim, D.J.Seong, J.Y.Lim, and K.H.Chung, Appl. Phys. Lett. V83, p4725 (2003).

PS-TuP12 Simulation Study of Plasma Display Panel Micro Discharge at Atmospheric Pressure Regime*, **S. Mukherjee**, J.K. Lee,* Pohang University of Science and Technology, South Korea, S. Korea

Plasma display panels (PDPs) are high pressure micro discharges that are promising sources of light, ions and radicals. The cell dimensions in a conventional PDP are in the order of microns and operated at high pressures of 400-500 Torr. In our study we operate the panel at pressures in atmospheric range to study the distinction in the characteristics of the discharge. At constant pd value of 10 Torr-cm by increasing pressure p (ranging from 0.5 to 2 atm) and reducing gap length d (up to 60 microns), we observe similar discharge characteristics as of conventional PDP. The Xe concentration is varied from 10 to 50 percent under such pressures in the Ne-Xe gas mixture that is used in our simulation, to observe the predictable increase in the driving voltage and anomalous behavior of the emission spectra at the dielectric at such pressures and concentrations. It is also beneficial to the study the variation in efficiency, power consumption, density of electrons and metastables at such pressures and concentrations. The UV emission line spectra for excited Xe (3P1) are also affected at such high pressures. We also investigate the difference in the discharge characteristics in the presence and absence of radiation trapping@footnote 1@ and dimers@footnote 2@ in our fluid simulation. @FootnoteText@ @footnote 1@H.C. Kim, S.S. Yang, and J.K. Lee, J. Appl. Phys. 93(12), 9516 (2003).@footnote 2@K. Wojciechowski et.al, Radiation Physics and Chemistry 99, 85(6).

PS-TuP13 Effects of a Pulse Duty Ratio in Dual Frequency Capacitively Coupled Plasma and a Magnetic Field by a Three-Dimensional Charge-Up Simulation*, **S.J. Kim**, S.J. Wang,* Pohang University of Science and Technology, South Korea*; H.J. Lee,* Pusan National University, South Korea*; J.K. Lee,* Pohang University of Science and Technology, South Korea, S. Korea

A dual frequency Capacitively Coupled Plasma (CCP) which independently controls an ion flux and an ion energy is widely used for typical dielectric etching. However, it induces a charge-up damage, which has a harmful effect on the reliability of a device. We have studied charge-up effects in the dual-freq. CCP by a three-dimensional charge-up simulator. In the charge-up simulator [1], the Laplace equation for an electric field calculation is solved. The energy and the angle distributions of ions and electrons used as input parameters are obtained in the dual-frequency CCP by a one-dimensional Monte-Carlo Particle-in-Cell (PIC) simulation [2]. In the dual-frequency CCP, 2MHz pulse is used as a low frequency source and a high frequency is 27MHz. Pulse conditions such as a rising time and a sustain time of the pulse which influence a plasma density and an electron temperature are investigated. The charge-up damage is produced by different motions of ions and electrons. Thus, negative ions as a substitute for electrons reduce the charge-up damage. A pulse duty ratio controls the ratio of a positive ion flux to a negative ion flux in oxygen plasma. Optimal conditions of a pulsed discharge are obtained in order to reduce the charge-up damage and to increase the etch rate. A magnetic field is applied to substrate as a method for the reduction of the charge-up damage. The effect of the magnetic field on the substrate is investigated by the 3D charge-up simulation. This work is supported by the national program for Tera-level nanodevices in Korea Ministry of Science and Technology. [1] H.S. Park, S.J. Kim, Y.Q. Wu, and J.K. Lee, "Effects of plasma chamber pressure on the etching of micro structures in SiO2 with the charging effects", IEEE Trans. Plasma Science 31 (4), 703 (2003). [2] H.C. Kim, J.K. Lee, and J.W. Shon, â?oDischarge asymmetry induced by the pulse radio-frequency currentâ?�, Appl. Phys. Letts. 84, 864 (2004).

PS-TuP14 Time and Space Resolved Optical Emission Spectrogram of Inductively Coupled Chlorine Plasmas for Etch Process*, P.H. Huang,* ***T.L. Lin,*** National Tsing Hua University, Taiwan*; K.C. Leou,* National Tsing Hua University, Taiwan, ROC*; H.J. Ding, C. Lin,* National Tsing Hua University, Taiwan

The applications of optical emission spectroscopy as a quantitative plasma diagnostic technique are powerful tools with the highest benefit being noninvasive measurements of chemically complex discharges. The major task of this work@footnote 1@ was to develop a time and space resolved spectrograph measurement systems of plasma induced emissions from processing plasmas, such as plasma etchers. We used the optical emission tomography (OET) technology and optical emission actinometry (OEA) principles to measure Cl@super +@, Cl and Cl@sub 2@ density variations with space and time in a high density inductively coupled plasma (ICP). The measurement system consisted of a 3 channels spectometer and a motor driven scanning stage mounted on a slot shaped vacuum window on the processing chamber. The optical emissions were sampled by a optical fiber adaptor mounted on the motorized stage which can scan across the chamber horizontally. Due to the configuration of the scanning system, the sampled optical emissions from the plasma are not at the same point in the space-time phase space. A polynomial interpolation method was employed to obtain spectra intensities of Cl@super +@, Cl and Cl@sub 2@ at the same point in space-time phase space. Consequently, we could analyze the spatial-temporal transient behaviors. Experimental results show that spatial profiles of Cl@super +@, Cl, Cl@sub 2@ densities evolve in significantly different trend during the etch process. This might be results from the generation of etch products, SiCl@sub x@, and changing of chamber wall conditions. @FootnoteText@ @footnote 1@ This work has been supported by the National Science Council, ROC, grant no. NSC 92-2218-E-007-019.

PS-TuP15 Controlling of UV Radiation Damages using On-wafer Monitoring Technique*,* ***M. Okigawa,*** *Y. Ishikawa, Y. Katoh, S. Samukawa,* Tohoku University, Japan

Gate insulator for metal-insulator silicon (MIS) devices needs high breakdown voltage, low leakage current and low interface states for robust semiconductor devices. Generation of electron-hole pairs in dielectric film as the gate insulator was measured by using our developed on-wafer monitoring technique during the plasma etching processes. To detect the generation of electron-hole pairs by plasma-induced electrical current in the insulator, we developed four types of on-wafer monitoring devices. Each device has an insulator structure such as single SiO@sub 2@ film, single Si@sub 3@N@sub 4@ film, SiO@sub 2@ film stacked on Si@sub 3@N@sub 4@ or Si@sub 3@N@sub 4@ film stacked on SiO@sub 2@. We found that the electron-hole pairs were generated in the insulators by the plasma-induced ultraviolet (UV) photons. We use three gas mixtures (CF@sub 4@+O@sub 2@, C@sub 2@F@sub 4@+O@sub 2@ and C@sub 4@F@sub 8@+O@sub 2@) to vary the wavelength of the emitted UV light in the plasma. The induced current depended on the UV wavelength meaning gas chemistry and the on-wafer monitoring device structures. In the SiO@sub 2@ film, CF@sub 4@ induced the most current of the three gas mixtures because CF@sub 4@ emitted the strongest intensity of the UV light having shorter wavelength than 140 nm as the SiO@sub 2@ band gap of 8.8eV. On the other hand, in the case of the Si@sub 3@N@sub 4@ single film, C@sub 4@F@sub 8@ has larger plasma induced current than other two gas mixtures. C@SUB 4@F@sub 8@ has the most intense UV lights of shorter than 250 nm that is the band gap of Si@sub 3@N@sub 4@, 5.0eV. Additionally, we evaluated the plasma-induced current using multi-layer insulator devices that consisted of both SiO@sub 2@ and Si@sub 3@N@sub 4@. The structure of Si@sub 3@N@sub 4@ on SiO@sub 2@ drastically reduced the plasma-induced current as compare with the structure of SiO@sub 2@ on Si@sub 3@N@sub 4@. This might be caused by the difference of the band-energy structure between them.

PS-TuP16 Diagnostic Studies on a H@sub 2@-N@sub 2@ Inductively Coupled Plasma for Plasma-Assisted Atomic Layer Deposition*,* ***S.B.S. Heil,*** Eindhoven University of Technology, The Netherlands, Netherlands*; E. Langereis, R. Engeln, M.C.M. van de Sanden, W.M.M. Kessels,* Eindhoven University of Technology, The Netherlands

A new reactor has been constructed for plasma-assisted atomic layer deposition (PA-ALD) of single-element metals and metal nitrides. Besides a vapor dosing system, the reactor consists of an inductively coupled plasma in which H, N, and NH@sub x@ radical species can be produced by operating the plasma on H@sub 2@, N@sub 2@, or NH@sub 3@ and mixtures of these gases. These radicals and possibly other activated neutrals can be used for abstraction of ligands from adsorbed metal halide precursor gases such that also non-binary materials can be deposited by ALD. We have investigated H@sub 2@ and N@sub 2@-H@sub 2@ plasmas by double Langmuir probe measurements and by optical emission spectroscopy. These measurements have been carried out for different plasma conditions and flow ratios while the OES data have been taken at different spatial positions. With OES we have observed the different atomic hydrogen lines as well as the H@sub 2@ Fulcher bands and the first and second positive systems of N@sub 2@. With the Langmuir probe measurements typical electron and ion densities of ~10@super 10@ cm@super -3@ and electron temperatures within the range of 2.5-3 eV have been obtained in the downstream region of the plasma. Currently, the first PA-ALD experiments of Ti and TiN films (e.g., for Cu diffusion barriers) are being carried out using the combination of TiCl@sub 4@ and H@sub 2@(-N@sub 2@) plasmas. The resulting film properties obtained under the different operating conditions will be compared with the results from the plasma studies.

PS-TuP17 Estimation of the Surface Potential Generated on Semiconductor Dielectric Materials Upon Exposure to Vacuum Ultraviolet Radiation Using a Monte-Carlo Simulation@footnote 1@*,* ***G.S. Upadhyaya,*** *J.L. Shohet, J.L. Lauer,* University of Wisconsin-Madison

The effect of Vacuum Ultraviolet Radiation (VUV) on dielectric materials during plasma processing is significant. During processing, charge deposited on the material due to the plasma can adversely affect device reliability. Plasma-generated VUV radiation can beneficially deplete the charge by temporarily increasing the conductivity of the dielectric.@footnote 2@ This effect has been attributed to photoemission and photoconduction currents generated by VUV exposure.@footnote 3@ This can result in a positive surface charge, which is measured using a Kelvin Probe. However, the transport of electrons and holes generated by VUV radiation inside the dielectric is not well understood. To this end, we utilize a Monte-Carlo code, which includes the different processes that an electron undergoes once it has been released from an atom by a VUV photon. The code includes Rayleigh scattering of the incident VUV photons inside the dielectric, photoelectric absorption, and elastic and inelastic scattering of photoemitted electrons. The statistical data obtained from the simulation, such as the backscattering percentage for the electrons, the absorption coefficient of the electrons inside the dielectric, and the distances traveled by the electrons and holes is used to compute the surface potential generated on the dielectric. The simulation estimate is found to be in very good agreement with the experimental measurements made using the Kelvin Probe technique. The cross sections used for the various processes in the VUV regime are based on previous work where available. The remaining cross sections are estimated from experimental measurements in which synchrotron radiation is incident on the dielectric. @FootnoteText@ @footnote 1@ Supported by NSF under grant DMR-0306582. The UW Synchrotron is funded by NSF under grant DMR-0084402.@footnote 2@ C. Cismaru and J.L. Shohet, Appl. Phys. Lett. 76, 2191 (2000)@footnote 3@ J.L. Lauer, J.L. Shohet, et. al., J. Appl. Phys. 91, 1242 (2002).

PS-TuP18 Induced Charge during Vacuum-Ultraviolet Irradiation of Al@sub 2@O@sub 3@, SiO@sub 2@, and Si@sub 3@N@sub 4@@footnote 1@*,* ***J.L. Shohet,*** *J.L. Lauer, R.W. Hansen, G.S. Upadhyaya, R.D. Bathke, K. Kukkady, J.M. Kalwitz,* University of Wisconsin-Madison

Plasma damage, contamination, and thermal budget are key concerns in the microelectronics industry. In particular, dielectric charging plays a key role in processing damage of semiconductor devices. During the last decade, plasma-induced damage research has mainly focused on the role of charged particles in the plasma with little or no consideration being given to photon bombardment. VUV radiation with energies in the range of 4-30 eV can induce charge on electronic materials. Radiation charging of Si wafers coated with 3000A of Al@sub 2@O@sub 3@, SiO@sub 2@, and Si@sub 3@N@sub 4@ from synchrotron VUV exposure with photon fluxes in the range of 10@super 9@-10@super 13@ photons/sec cm@super -2@ was measured. The total charge induced on the dielectrics during VUV exposure, which can be measured with a Kelvin Probe, consists of charge due to photoemission and electron-hole pair creation. The photoemission current and substrate voltage were monitored during each exposure for various bias voltages. For photon energies of 7-21 eV, the integral of photoemission current was compared to the net charge measured with the Kelvin probe which allows us to separate the charging affects of photoemission from that of electron-hole pair creation within the dielectric. Since the threshold photon energy for photoemission is higher than that for electron-hole pair production, it is seen that photoemission can be minimized if the photon energies are below the threshold energy. This produced the possibility to reduce dielectric charging, especially that induced by electron-shading effects during plasma etching of high aspect-ratio devices, by providing a safe way to discharge these structures and, thus, minimize plasma-charging damage. The enhanced conductivity may benefit etching properties such as reduction of notching, sidewall bowing, and trenching. @FootnoteText@ @footnote 1@This work is supported by NSF under grant DMR-0306582. The UW Synchrotron workis funded by NSF under grant DMR-0084402.

PS-TuP19 Electrical Characteristics of Linear Internal-type Inductively Coupled Plasmas Source*, G.Y. Yeom,* Sungkyunkwan University, South Korea, Korea*; **K.N. Kim**, S.J. Jeong,* Sungkyunkwan University, South Korea

Inductively coupled plasma ICP sources have been studied extensively in the past ten years as candidates for advanced etch and deposition processing tools. Although ICP plasma sources have many advantages, the plasma generated is inherently non-uniform due to the antenna standing wave effect, when the plasma source is scaled to large size comparable to the driving rf wavelength. In this study, large-area plasmas with inductive coupling of extended internal linear- antennas have been proposed a promising candidate for an efficient high-density plasma source. The process chamber was designed as a rectangular mainly for 4th generation FPD application and was made of stainless steel. The inner size of the chamber was 1020mm*830mm. The characteristics of the plasmas were measured using a quadrupole mass spectrometer and a Langmuir probe located on the sidewall of the chamber. And the electrical characteristics of linear antennas were measured using an impedance probe. The results showed a strong relationship between the antenna design and plasma characteristics such as density and uniformity. Under an optimized antenna design, the uniformity of the Ar@super+@ ion density less than 4% could be obtained while maintaining high plasma densities on the order of 2.67*10@super11@cm@super-3@.

PS-TuP20 Effects of Water Vapor on Plasma Parameters in Processing Plasmas*, **Y. Ichikawa**, M. Narita, K. Sasaki,* Fuji Electric Device Technology Co., Ltd., Japan

We have studied the effects of a trace amount of water vapor on the properties of processing plasmas by numerical analysis. In plasma processing for semiconductor applications such as sputtering and plasma CVD, oxygen is easily incorporated in the deposited films or in the ambience of plasma and seriously influences the properties of films and the performance of semiconductor devices. The principal source of oxygen is water vapor emitted from the wall of reaction chambers. Thus it is very important to understand the behavior of water vapor in processing plasmas. With a view to understanding the effect of water vapor on the processing plasma, we made a modeling of Ar positive column plasma; Ar is most popularly used for plasma processing in all the rare gases. The analytical method employed here is based on a positive column theory of Ichikawa and Teii.@footnote 1@ In the modeling, we took into account 6 ion species, Ar@super +@, Ar@sub 2@@super +@, H@sub 2@O@super +@, H@sub 3@O@super +@, OH@super +@, H@super +@ and meta-stable Ar. The reaction scheme among these species is very complicated, but assuming a small amount of H@sub 2@O in Ar, we can simplify the reaction system. The obtained results show that the abundance ratios of H@sub 2@O@super +@ and H@sub 3@O@super +@ become comparable to that of Ar+ even if a very small amount of H@sub 2@O, e.g. less than 1%, is added in Ar; these H@sub 2@O related ions increase with increasing gas pressure and chamber size. We will present the details of ion-molecule reactions used in the modeling for the Ar-H@sub 2@O plasma and numerical results. @FootnoteText@ @footnote 1@Y. Ichikawa and S.Teii, J. Phys. D, 13, 2031 (1980).

PS-TuP21 Evaluation of Germicidal Effect by Plasma Sterilization System in Air*, **J.H. Choi**, H.K. Baik, J.C. Park, D.W. Han,* Yonsei University, Korea

Atmospheric pressure(AP) plasmas can sterilize almost all kinds of bacteria because many germicidal species, such as atomic oxygen, hydroxyl radical and ozone etc. are generated during AP plasmas. So AP plasmas are proper process for application to air cleaner or sterilizer. The aim of this paper is to evaluate a germicidal effect by plasma sterilization system in air. For this experiment, we modified the inhalation exposure system used for experiment to infect animal. By the nebulizer in our plasma sterilization system, aerosol attached to bacteria in culture media was generated, and therefore we could make a proper process to evaluate the germicidal effect of air cleaner including AP plasma system. We made 3 types of plasma reactor and these are dielectric barrier discharge, surface barrier discharge and pack-bed discharge type. We used alumina and copper for dielectric and electrode material respectively. And in many sorts of bacteria, e-coli, pseudomonas aeruginosa and bacillus subtillus were used for this sterilization experiment. For analysis of the relationship between sterilization results and chemical species generated in discharge, we used optical emission spectroscopy (OES) and we checked emission spectra by atomic oxygen (394.2nm and 436.8nm) and O2+ ion (631.4nm). From these results, we concluded that our AP system is very effective to evaluate germicidal effect.

PS-TuP22 Extending the "Winters and Coburn Method"@super 1@ to Plasma Propellant Interactions*, **R. Valliere**, R. Blumenthal,* Auburn University

There has been a significant interest in the use of plasmas to ignite propellants, specifically for large bore artillery. A short, reproducible ignition delay and a reduced temperature dependence are the most important advantages of plasma ignition over conventional ignition. The fundamental interactions of plasma and the propellant have been investigated using the experimental modeling method, pioneered by Winters and Coburn,@super 1@ that is responsible for our current understanding of the etching of semiconductors. The erosion rates of sprayed-on films of RDX and HMX have been measured in inert and reactive plasmas, with both negative and positive sample biases in order to select ion and electron bombardments of the propellant surface. No significant erosion rate was observed in argon plasmas with zero or any positive applied bias, indicating that erosion by electron bombardment alone is not important. Under large negative bias, ion bombardment conditions, a small erosion rate was observed. The minimum of erosion rate found for all positive and zero sample biases in hydrogen plasmas was 100x the erosion rate of the negatively-biased argon plasmas. Above a threshold of approximately -250V DC bias, the erosion rate in the hydrogen plasmas increases by another order of magnitude. The fact that the etch rates in the hydrogen plasmas are all much greater than the sputter rate of the argon plasmas (observed at large negative bias) indicates that the process in hydrogen plasmas is chemically enhanced and has strong synergistic effects. Detailed results of the individual roles and synergistic interactions of ions, H radicals and electrons with the propellant surface will be presented. @FootnoteText@ @footnote 1@H.F. Winters and J.W. Coburn, J. Vac. Sci. Technol, B 3(5), 1376 (1985).

PS-TuP25 The Fate of Nitrogen in Plasma Polymerization Revealed by NEXAFS*, **A.G. Shard**, S.L. McArthur,* University of Sheffield, UK*; J.D. Whittle,* Plasso Technology, UK*; A.J. Beck, R.A. Talib,* University of Sheffield, UK*; N.A. Bullett,* University of Sheffield, UK, United Kingdom*; P.N. Brookes,* University of Sheffield, UK

The determination of plasma polymer chemistry is often rather difficult due to the large numbers of candidate functional groups. Conventional analytical methods such as X-ray photoelectron spectroscopy (XPS) and infrared (IR) spectroscopy have limitations, particularly with regard to nitrogen containing plasma polymers. In these polymers there are potentially a number of functional groups which cannot be distinguished from amines by XPS such as aromatic amines, pyridinic structures, imines and nitriles. With IR spectroscopy there are also difficulties in identifying some of these species, coupled to a lack of quantification. The presence of such groups may impair the effectiveness of plasma polymerized amines in their ability to interact electrostatically and to be available for imine coupling reactions so their detection is a matter of some importance. Near edge X-ray absorption fine structure (NEXAFS) can easily distinguish the presence of the unsaturated species mentioned above. We have applied this technique to a range of nitrogen containing plasma polymers and show that the ultimate fate of nitrogen, particularly at high powers, is to produce nitrile groups. We have studied saturated and unsaturated amine and amide containing monomers and a copolymerisation of allylamine and acrylic acid. This study has implications for potential new uses of such materials and indicates that the long term oxygen incorporation into aminated plasma polymers may be due to hydrolysis of imine and nitrile groups.

Semiconductors

Room Exhibit Hall B - Session SC-TuP

Poster Session

SC-TuP1 Epitaxial Growth of GaN on Sapphire by RF-MOMBE*, S.Y. Kuo,* National Science Council, Taiwan, R.O.C.*; C.C. Kei,* National Science Council, Taiwan, Taiwan, R.O.C.*; C.K. Chao,* National Central University, Taiwan*; J.S. Chen,* National Science Council, Taiwan*; S.Y. Huang,* National Taiwan University, Taiwan*; **C.N. Hsiao**,* National Science Council, Taiwan, R.O.C.

A self-designed radio-frequency plasma metal organic molecular beam epitaxy (RF-MOMBE) system is developed to study III-nitride semiconductors. The surface morphologies and crystal structures were monitored by in-situ reflection high energy electron diffraction (RHEED). Up to 4 inches substrates of sapphire, silicon and other materials were available. Followed by substrate nitridation, a low temperature buffer layer was deposited to facilitate growth of III-nitride films on large lattice mismatched substrates. The III-nitride films were characterized by photoluminescence spectrometry, x-ray diffraction, scanning electron microscopy and transmission electron microscopy. The effect of growth temperature and III-V ratio on crystallinity and surface morphologies of III-nitride films was prominent. High quality III-nitride films were achieved by well optimized condition.

SC-TuP2 Comparison of Ga- and N-polar GaN Surfaces*, **R.P. Bhatta**, B.D. Thoms,* Georgia State University*; C.R. Eddy, Jr., R.T. Holm, R.L. Henry,* Naval Research Laboratory

Growth of wurtzite GaN(0001) thin films by metalorganic chemical vapor deposition (MOCVD) may produce either Ga- or N-polar surfaces resulting in differences in surface termination, electronic structure, and chemical reactivity. GaN surfaces of both polarities have been characterized, in particular by their reaction with atomic hydrogen and deuterium. Auger Electron Spectroscopy (AES) and Low Energy Electron Diffraction (LEED) showed that the surfaces were clean and ordered. Electron Energy Loss Spectroscopy (EELS) and High Resolution Electron Energy loss Spectroscopy (HREELS) were used to characterize the electronic and vibrational properties of the surfaces. After cleaning the N-polar surface by sputtering with 1 keV nitrogen ions and annealing to 900 @degree@C, HREELS showed Fuchs-Kliewer phonons, N-H stretching vibrations, and combination losses, which indicate that hydrogen is present on the surface after annealing. HREELS following exposure to atomic hydrogen (deuterium) confirmed the assignment of surface N-H (N-D) and showed no sign of surface Ga-H (Ga-D) species. In addition, heating to temperatures from 400 to 900 @degree@C was not sufficient to remove the surface N-H species. In contrast, HREELS of the Ga-polar surface after sputtering and annealing showed Fuchs-Kliewer phonons but not any adsorbate loss peaks, which indicates a hydrogen-free surface. HREELS following exposure to atomic hydrogen (deuterium) reveals Ga-H (Ga-D) stretching vibrations along with combination modes, but no N-H (N-D) vibrational modes are observed. Hydrogen is desorbed completely from this surface below 400 @degree@C. In addition to differences in surface termination and chemical reactivity, EELS was used to characterize differences in the electronic structure of the hydrogenated Ga- and N- polar surfaces.

SC-TuP3 Ohmic Contacts to AlGaN*, S.E. Mohney, H.J. Wang, **M.A. Horsey**,* The Pennsylvania State University*; B.A. Hull,* Cree, Inc.

Research on ohmic contacts to Al@sub x@Ga@sub 1-x@N of high Al fraction (x) is presented. The work was motivated by the requirements for low resistance ohmic contacts for short-wavelength devices. In the work on ohmic contacts to n-Al@sub x@Ga@sub 1-x@N with x = 0.6, we have achieved reproducible contact resistivities of 4 x 10@sup -6@ Ohm-cm@sup 2@ with V/Al/V/Au contacts, even without reactive ion etching prior to metallization. These contacts exhibit relatively smooth surface morphologies. We have also investigated the interfacial reactions in these contacts using transmission electron microscopy and Auger electron spectroscopy to provide more information on the mechanism for forming a low resistance ohmic contact. For contacts to p-Al@sub x@Ga@sub 1-x@N (x = 0.45), we have identified annealing conditions required to achieve ohmic contacts, and we discuss the need for passivation of the p-Al@sub x@Ga@sub 1-x@N surface in order to avoid degradation from exposure to light, due we believe to traps at the semiconductor surface. We also describe the relationship between the resistance of the contacts and the interfacial reactions between the contacts and p-Al@sub x@Ga@sub 1-x@N.

SC-TuP4 Fabrication and Properties of Thin Film Photon Sieve Diffractive Lens*, **N. Bradman**, H. Chung, M. Davidson, P.H. Holloway, K. Woo, D. Tanner, S. Selcuk, A. Hebard,* University of Florida*; O. Shenderova, A. Shenderova, G.E. McGuire,* International Technology Center

Photon sieves are diffractive lens that offer better focusing than Fresnel zone plates and are lighter weight and lower volume than refractive lens. The photon sieve lens in this study consists of a transparent substrate coated with an opaque metal thin film with a pattern of holes in a circular array. The size of the holes range from above to below the wavelength of light being focused. Fabrication of the photon sieve lens will be described, which consists of a thin electron beam metallization, pattern writing by electron beam lithography, and pattern development by reactive ion etching. In addition to significant reductions in weight and volume, photon sieves offer a larger field of view than refractive optics, but they suffer from poor transmission. Surface plasmon resonant coupling will be reported to improve the transmission by factors of two to five at the resonant wavelength. The coupling of the surface plasmon resonant structure with the photon sieve pattern will be discussed. Transmission data for traditional and modified photon sieves will be presented and compared.

SC-TuP5 Etch Characteristics of Sapphire using Inductively Coupled Plasmas*, **Y.J. Sung**, T. Jang, K.K. Choi, S.H. Chae, Y.H. Kim, J.S. Kwak, O.H. Nam, Y. Park,* Samsung Advanced Institute of Technology, South Korea

Sapphire has been widely used as a substrate for epitaxial growth of GaN-based optoelectronic devices due to its high chemical and thermal stability. Therefore it is essential to understand the dry etching technique in order to fabricate advanced optoelectronic devices. Recently, researches on the various etching of sapphire such as inductively coupled plasma etching, ion beam etching, chemical wet etching after ion implantation, reactive ion etching, etc. have been carried out and have focused on achievement of high etch rates and high selectivity over etch mask. In case of GaN-based laser diodes and light emitting diodes, various sapphire etching methods have been applied to techniques such as epitaxial lateral overgrowth(ELO) and lateral epitaxial patterned sapphire substrates(LEPS) to reduce dislocation density in GaN layer. However, until now there have been only a few works on the etching of sapphire and its properties. In this study, inductively coupled plasmas were used to etch sapphire. The effects of etch parameters such as gas combination of BCl@sub3@/ Cl@sub2@ and BCl@sub3@/Cl@sub2@/Ar, inductive power (400- 800Watts), bias voltage (-100--300Volts), and operational pressure (3-30mTorr) on the etch characteristics such as etch selectivity and etch properties of sapphire were investigated. To investigate the etch mechanism of sapphire, optical emissions from the plasmas during the etch process were monitored in situ and the sapphire surface composition after the etching was observed by X-ray photoelectron spectroscopy.

SC-TuP6 Exact-Exchange-Based Quasiparticle Calculations of II-VI Compounds and Group III Nitrides*, **P. Rinke**,* Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany*; A. Qteish,* Yarmouk University, Jordan*; J. Neugebauer,* University of Paderborn, Germany*; M. Scheffler,* Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany

We present a systematic ab initio study of the electronic structure for a wide range of II-VI compounds and group III nitrides in the zinc-blende structure. The challenge from a computational point of view is to capture the exchange-correlation effects arising from the shallow semicore d-electrons of the cation, which we explicitly treat as valence states in our pseudopotential approach. In order to correctly describe the dominant exchange interaction we apply density-functional theory (DFT) in the exact-exchange (EXX) approximation. Although the EXX Kohn-Sham bandstructure compares well with experiment for standard semiconductors@footnote 1@ the bandstructure as measured by photoemission is a property of the excited system. We therefore apply many-body perturbation theory in the GW approximation to the EXX groundstate. The hirarchy of our approach allows us to systematically investigate the role of exchange and correlation in these materials from first principles. Our results show that it is crucial to treat exchange and correlation on the same footing at every stage. To achieve this in our EXX calculations we employ the newly developed EXX-pseudopotentials@footnote 2@. Furthermore we obtain GW bandstructures in very good agreement with existing all-electron GW calculations. Our results indicate that, in contrast to common believe, a pseudopotential approach including only the d-electrons of the semicore shell in question, is sufficient to accurately describe the electronic structure if treated in the EXX+GW formalism. @FootnoteText@ @footnote 1@ W. G. Aulbur et al, Phys. Rev. B 62, 7121 (2000)@footnote 2@ M. Moukara et al, J. Phys.: Condens. Matter 12, 6783 (2000) .

SC-TuP7 Transparent Conducting Oxides Based on ZnO by Reactive Sputtering*, **M.A. Santana-Aranda,*** Instituto Mexicano del Petroleo, México*; M. Meléndez-Lira,* Centro de Investigación y Estudios Avanzados, México, Mexico*; M. Becerril-Silva, S.J. Jiménez-Sandoval,* Centro de Investigación y Estudios Avanzados, México

Transparent conducting oxides have a broad variety of applications in the electric and optoelectronic industries. Applications like conducting window material for solar cells as well as active layers of LEDs and laser diodes emitting in the UV. We have employed reactive sputtering to deposit ZnO and Al:ZnO thin films on glass substrates. The target was formed with zinc and aluminum circular plates; we controlled the aluminum content changing the ratio of Al/Zn areas. Surface morphology and aluminum content were monitored with a scanning electron microscope. X ray diffraction and Raman spectroscopy measurements were performed to monitor the crystalline structure of the films. The energy of the absorption edge was monitored by optical transmission measurements. The changes observed in the absorption edge are related with the changes in the aluminum content of the films. Resistivity of the films was determined by electrical measurements, these results are also well correlated with the aluminum content.

SC-TuP8 XPS and UPS Study of ZnO:N Thin Films*, **C.L. Perkins,*** National Renewable Energy Laboratory*; X. Li,* University of Texas at Arlington*; S. Asher, T.J. Coutts, S.-H. Lee,* National Renewable Energy Laboratory

There are strong motivations for obtaining nitrogen-doped p-type ZnO, including the possibilities of air-stable, high quality UV lasers, detectors, and efficient photocatalytic water splitting. Problems remain with the growth of this material however. Reproducibility of conductivity type is difficult, and the distributions and identities of nitrogen species in N-containing ZnO films are not well known. Although theory predicts that N can be incorporated in at least two different states, one of which, N@sub 2@ occupying a position on the oxygen sublattice (N@sub 2O@) should be a double shallow donor, and the other, NO, being the desired acceptor, there have been few determinations of the chemical states of nitrogen in ZnO:N materials. In order to gain a better understanding of their chemical and electronic properties, we have examined via XPS and UPS thin films of ZnO:N produced by two different methods. MOCVD films were grown using diethylzinc and nitric oxide. Sputtered films were produced with a Zn target and a mixture of O@sub 2@ and N@sub 2@. Core level photoemission shows that the films contain 0.5-2.5 % nitrogen, and that the nitrogen occupies at least four different chemical environments. With UPS the relative positions of the films' valence bands are determined with respect to the Fermi level. Results from the thin polycrystalline films are compared to initial results obtained on ZnO(0001) single crystals reacted in UHV with nitric oxide, and with data obtained from N-implanted Zn foil. Definitive XPS peak assignments are made for N@sub 2O@, N@sub O@, and two other nitrogen chemical states that have not previously been identified in ZnO:N.

SC-TuP9 Electrical Characteristics of Al-doped ZnO (Al-ZnO) Films and their Application to Al-ZnO/p-Si Solar Cells*, **T. Ichinohe,** S. Masaki,* Tokyo National College of Technology, Japan*; K. Kawasaki,* TDY Co., Ltd., Japan

We fabricated aluminum doped zinc oxide (Al-ZnO) films by DC-magnetron sputter-deposition. The films showed n-type semiconductor characteristics: they were electron carriers with a negative coefficient of resistivity. We attempted to fabricate a p-n junction structure using Al-ZnO films formed on a p/p@super +@-Si epitaxial substrate. The Al-ZnO/p-Si structure showed rectified I-V characteristics, indicating a p-n junction has been fabricated. The photocurrent for reverse bias increased to several hundred times higher than dark current when a halogen lamp irradiated its surface. The open circuit voltage (V@sub oc@) increased when the halogen lamp power was increased, and the value saturated at about 0.2 V. We infer that the value of V@sub oc@ is appropriate for built-in potential (0.3 eV) in the interface of Al-ZnO/p-Si, as estimated by the Kelvin-probe work function measurement system. Energy efficiency of the Al-ZnO/p-Si structure was about 1.2%, as estimated by the standard quasi-solar light exposure system. Reducing the resistivity of Al-ZnO films and the contact resistance of the cell structure can further increase the energy efficiency.

SC-TuP10 Supermagnetron Plasma CVD of Amorphous CNx:H Films Using Rf Power-Ratio Control*, **H. Kinoshita,** R. Ikuta, K. Sakurai,* Shizuoka University, Japan

Amorphous CNx:H films were deposited on lower electrode using i-C4H10/N2 supermagnetron plasma CVD. @footnote 1@ By a control of rf power-ratio, hard and soft CNx:H films were deposited at upper electrode rf power of 800W. Above the lower electrode rf power (LORF) of 40W, CNx:H films became hard and opaque. Below LORF of 20W, however, CNx:H films became soft and transparent. The optical band gap of hard film was below 0.8eV and that of soft film was above 1.9eV. Hardness of hard film was above 19GPa and that of soft film was about 7GPa. Electrical resistivity of hard film was low and that of soft film was high. Soft films showed white photoluminescence. @FootnoteText@ @footnote 1@H.Kinoshita and T.Murakami, J.Vac.Sci.Tecnol.A 20, (2002) 403.

Advanced Surface Engineering
Room Exhibit Hall B - Session SE-TuP
Poster Session

SE-TuP1 Ab-Initio Structural Properties and Stress-Deformation Analysis by Rheological Modeling of Fracture of Diamonds-Containing Nanocomposites*, M.V. Kireitseu,* University of New Orleans*; **I.O. Nedavniy,*** Institute of Strength Physics and Materials Science, Siberian Branch of Russian Academy of Sciences, Russia

The principal goal of the paper is to study fundamentally pure interfaces diamond-like C / metal or polymer structure (matrix). Diamonds nanoclusters with effective sizes between 2 nm and 50 nm were used. The present work describes study of stable atomic structure of diamond-like nanoclusters embedded into metal or polymer matrix. Diamond nanoparticles have spherical, fullerene or pyramidal-type shapes and diamonds fibers as well. Local structure deformation (rearrangement) of diamonds/metal interfaces was principal object of researches. Energy or band structure and density of electronic states analysis were investigated. Possible defect or surface states were described. Ab initio LCAO (HF or DFT) schemes, LASTO (Linear augmented Slater-type orbital method), MLASTO (Modified linear Slater-type orbital method), ab initio DFT LDA (FLAPW, LASTO, pseudopotential) super cell schemes and semi empirical LCAO (AM1, PM3, PM5, etc.) methods were used for diamonds nanoclusters with effective size less than 2 nm. It was found that embedded diamonds might be reconstructed in a fullerene-like manner. Fundamental parameters for tight-binding and molecular dynamics calculation schemes were further based on computer simulation at each direction can be easily developed for better understanding and faster calculations. Study of size dependent mechanical and structural properties revealed at what scale principal fundamentals may give reliable explanations at examining fracture mechanics of nanostructured composites. We also present was to present the modified linear augmented Slater-type orbital method (LASTO) for solving Schrodinger's equation in nanodiamonds crystals with arbitrary atoms per unit cell. It follows to expect this method will allow more efficiently calculating an electronic band structure and structural energy difference for vary transition nanocomposites. As a result overlap matrix and hamiltonian matrix elements were derived in details.

SE-TuP2 Field Emission Enhancements from C-implanted Molybdenum*, **N.D. Theodore,** R.A. Outlaw, B.C. Holloway, D.M. Manos,* College of William and Mary

The vacuum microelectronic industry is developing large, compact field emitter arrays in high-brightness devices for flat panel displays and microwave tubes. Refractory carbides are materials of interest due to their reduced work function, stable emission, high current capability, and robustness. The purpose of this study was to better understand field emission enhancements observed in molybdenum carbide by comparing it to pure molybdenum. According to Fowler-Nordheim (FN) theory, field emission is determined by two parameters, the work function of a material and its surface roughness. Slope-intercept plots of the resulting FN data are then used to separate the effects of these variables. In this experiment, we deposited molybdenum onto both flat silicon samples and triangular silicon gratings that possessed a tip radius of approximately 10 nm. We then created molybdenum carbide by implanting carbon using plasma immersion ion implantation. Carbide formation was verified using XPS; both the C1s peak and the Mo3d peaks were shifted. Depth AES analysis determined that the carbon-implant extended ~45nm from the surface. The field emission results quantify the observed differences in work function and in emission current stability, and correlate these to variations in surface layer compositions and geometry. Moreover, flat samples did not exhibit repeatable electron emission. We conclude that in flat samples, field emission from surface defects dominates the measured emission current, and this mechanism is not explained by Fowler-Nordheim theory.

SE-TuP3 Chemisorption to the Oxide Surface of Aluminium Metal: The Competing Roles of Hydroxide Formation and Adventitious Contamination*, **M.R. Alexander**,* The University of Nottingham, UK*; G.E. Thompson,* UMIST, UK

An understanding of the interaction of organic functionalities with the surface of aluminium is required for development of a range of application areas including environmentally friendly adhesion promoters, superhydrophobic architecture, MEMS and NEMS. Formation of numerous types of organic monolayer on aluminium has been reported in the literature, the first of which predates that of alkane thiols on gold.@footnote 1@,@footnote 2@,@footnote 3@ Whilst the instability of the aluminium oxide surface in ambient conditions is widely recognised, quantification of the changes in surface hydroxyl group concentration and carbonaceous contaminant from the ambient atmosphere have only recently been achieved using X-ray photoelectron spectroscopy (XPS).@footnote 4@,@footnote 5@ Previous work has identified the significant influence of an ambient laboratory atmosphere on assembly of alkyl carboxylic and phosphonic acid monolayer.@footnote 6@,@footnote 7@ Here, we investigate the influence on chemisorption from dilute solutions of such molecules using controlled atmospheric exposure prior to assembly. The order of the resultant SAMs is used as a relative measure of the reactivity of the surface to the headgroups. Water contact angle, IRRAS and XPS are used to provide information on the chemistry of the oxide surface and the order the monolayer assembled onto this surface. Differences are rationalised using the competitive processes of hydroxyl adsorption site formation and adventitious contamination blocking of such sites developed in the earlier work. @FootnoteText@ @footnote 1@ Bigelow, W et al. Colloid Sci 1946; 1: 513.@footnote 2@ Timmons, C, Zisman, W. JPhysChem 1965; 69: 984.@footnote 3@ Allara, DL, Nuzzo, RG. Langmuir 1985; 1: 45.@footnote 4@ Alexander et al. SIA 2000; 29: 468.@footnote 5@ Alexander et al. SIA 2003; 35: 649.@footnote 6@ Alexander, MR et al. ASST:ATB Metallurgie, Brussels, 2004; 60.@footnote 7@ Pertays, K et al. SIA In Press.

SE-TuP4 Microstructure and Properties Changes in CrN Films Influenced by an Implanted Cr Interlayer*, H.-Y. Chen,* National Tsing Hua University, Taiwan*; **S. Han**,* National Taichung Institute of Technology, Taiwan*; H.C. Shih,* National Tsing Hua University, Taiwan

A chromium interlayer was implanted in (100) silicon using a metal vapor vacuum arc ion implanter, and then CrN films were deposited by cathodic arc plasma deposition. Two types of the CrN films denoted as CrN/Cr/Si (with an implanted Cr interlayer) and CrN/Si (without an implanted Cr interlayer). XRD patterns revealed the presence of CrN (220) preferred orientation for both cases, indicating that regardless of whether the films included a Cr interlayer, the preferred orientation and the columnar structure of CrN films were unchanged. But the interlayer induced finer grain structure and reduced the residual stress of the films from -8.1 GPa to -2.8 GPa, which relaxed by up to 65%. Moreover, the CrN films with a Cr interlayer were less hard and exhibited a higher electrical resistivity than those without. Both specimens were annealed at 500°C for 2 h in an N@sub 2@/H@sub 2@ atmosphere to elucidate the thermal stability of the CrN film. The CrN/Si revealed a phase transformation from CrN to Cr@sub 2@N during annealing, which is due to largely stress relaxation in the film. A implanted Cr interlayer can effectively relax the residual stress in CrN films and prevent a occurrence of phase transformation during annealing. The correlation between the properties and microstructure of the CrN film is also discussed.

SE-TuP5 Oxidation Behavior of Titanium Nitride Films*, **H.-Y. Chen**, H.C. Shih,* National Tsing Hua University, Taiwan

TiN films have been a universal coatings due to their high melting points, extreme hardness, high chemical stability, golden color and so on, and the oxidation of films occurs in the hostile environmental. The oxidation mechanism of TiN films has investigated by their crystal structure and morphology using XRD and Raman scattering spectroscopy and FESEM. TiN films were synthesized by using cathodic arc plasma deposition technique because its high ionization ratio, fast deposition rate. After films deposition, the films were annealed in static air at 500°C to 800°C for 2 h. The XRD and Raman spectra indicated that the rutile TiO@sub 2@ was identified above 600°C and its relative intensity rapidly increased with temperatures. The films completely oxidized into rutile phase above 700°C. The as-deposited TiN films were columnar structure. Nevertheless, the oxide layer appeared on the top of columnar TiN films above 600°C. Furthermore, the microstructure of the oxide was porous with the pore size of several nanometers within the oxide layer at 600°C. As increasing annealing temperature, the oxide morphology possessed elongated grain structure with the aspect ratio of ten and the pore size within the oxide layer ranged in several ten nm, which indicated the densification occurring. Form the results, the oxide layer obvious grow inward with temperatures, which indicates the oxidation of TiN films is inward oxidation, meanwhile the oxide thickness was measured with temperature and the active energy for the oxidation was deduced, which was 110±10 kJ/mol.

SE-TuP6 Effect of Ion Irradiation during Deposition on the Structure of Alumina Thin Films Grown by Plasma Assisted Chemical Vapour Deposition*, **D. Kurapov**, O. Kyrylov, J.M. Schneider,* RWTH Aachen, Germany

Alumina thin films deposited by plasma assisted vapour deposition were studied with respect to the structure and composition by X-ray diffraction and electron probe microanalysis, respectively. Alumina thin films were deposited on hot work tool steel AISI H11 at a growth temperature of 500 to 600 °C. The ion energy was affected by controlling the substrate power density from 2.7 to 6.6 W/cm@super 2@, which corresponds to the bias potential range from 720 to 905 V. Within the investigated process window the following characteristic phases could be identified : amourphous alumina, @gamma@-alumina, @alpha@-alumina as well as mixtures thereof. The alumina phase formation was found to be strongly influenced by deposition temperature and power density at the substrate. The influence of the power density is discussed with respect to the ion energy distribution, which is estimated based on the charge exchange model of Davis and Vanderslice.

SE-TuP7 Microstructural Evolution on the Oxidation of Arc Ion-plated TiN/(Ti,Al)N Superlattice Coatings*, **M.H. Shiao**,* National Science Council, Taiwan*; C.C. Wang, F.S. Shieu,* National Chung Hsing University, Taiwan

TiN/(Ti,Al)N superlattice coatings with a TiN interlayer were prepared by a dual-cathode arc ion plating system on AISI 304 stainless steel. Two targets of Ti and Ti@sub 50@Al@sub 50@ were used for the vertically opposited cathodes. Oxidation of the nitride-coated steel was carried out at the temperature of 800°C in air for 60 min. The microstructure and chemistry of the as-deposited and oxidized specimens was characterized by X-ray diffraction, scanning electron microscopy (SEM), transmission electron microscopy (TEM), and Auger electron spectroscopy (AES). XRD result shows that nitride coatings have strong (111) preferred orientation, and TiO@sub 2@ phase appeared in the oxidized specimen. Cross-sectional TEM reveals a TiN/(Ti,Al)N superlattice structure with a period of 7.7 nm examined by the selected area diffraction (SAD). In the oxidized specimen, there are dense amorphous Al@sub 2@O@sub 3@ layer and underlying porous TiO2 layer on the surface of the coating. Auger depth profiling of the oxidized specimens reveals that the Al element concentration near the surface layer is much higher than that in the nitride coating, and further confirmed the cross-sectional TEM results.

SE-TuP8 Development of Amorphous Layered Structures by Laser Irradiation for Enhanced Corrosion Resistance*, J.G. Hoekstra, P.M. Mackey, N. Ünlü, G.J. Shiflet, J.R. Scully, **J.M. Fitz-Gerald**,* University of Virginia

Al and Fe based amorphous materials attract attention for their desirable mechanical hardness and corrosion resistance. This study investigated the atomic scale relationships of amorphous layer formation as a function of chemistry and pulsed laser irradiation conditions in Al-Co-Ce and Fe-Mo-Cr-Mo-C-B alloys. The primary objective was to laser surface modify a continuous, homogenous, amorphous layer on a crystalline substrate. Irradiation of a material with a short laser pulse, 3-100 ns, establishes rapid melting and solidification velocities at the surface, 10@super 7@-10@super 8@ K/s and 10@super -1@-10@super 1@ m/s respectively. A KrF excimer laser (@lambda@=248 nm, 25 ns at FWHM, 15 Hz) operating with fluences ranging from 0-10 J/cm@super 2@ irradiated a target surface with corresponding velocity between 0-50 mm/s in a controlled atmosphere ranging from 50-500 mTorr. Characterization was performed by SEM, EDS, XRD, and electrochemical analysis. The resulting microstructures were correlated with electrochemical analysis and devitrification behavior.

SE-TuP9 Nanomechanical Testing Using Noncontact Acoustic Technique*, **O.G. Lysenko**, N.V. Novikov, V. Grushko,* Institute for Superhard Materials, Ukraine

The new techniques for noncontact measurements of acoustic waves and vibration parameters, such as atomic force acoustic microscopy and tunneling accelerometer have been developed the last years. We present the experimental technique that uses noncontact acoustic method to nanoscale surface characterization. A pulse laser is used to generate surface acoustic waves in a sample. Two SPM tips detect phase and amplitude of the acoustic waves. This approach makes it possible to measure acoustic transit time within small areas of a samles. From the velocity of the surface waves the elastic modulus can be culculated. Also it is possibly to identify the onset of plastic flow in the thin films. A theoretical model embracing the most significant features of wave phenomena at nanoscale level is described. Laboratory experiments have displayed results that are in agreement with those obtained from theoretical model.

SE-TuP10 Characterizations of the Surfaces of Shocked-Bi-Pb-Sr-Ca-Cu-O Superconductor Particles for a Magnetic Sensor*, **H.K. Kezuka**,* Tokyo University of Technology, Japan*; K.Y. Yamagata, M.I. Itoh,* Kinki University, Japan*; T.S. Suzuki,* Tokai University, Japan*; M.K. Kikuchi,* Tohoku Fukushi University, Japan*; T.A. Atou, M.K. Kawasaki, K.F. Fukuoka,* Tohoku University, Japan

Recently, there has been an increased need for a highly sensitive magnetic sensor. Bi-Pb-Sr-Ca-Cu-O(BPSCCO) oxide superconductors are very attractive material as a highly sensitive magnetic sensor in which magnetic sensitivity of the sensor is found to be about 27 %/(10 @super -4@ T) using BPSCCO powders pasted for constructing the magnetic sensor. Characteristics of BPSCCO superconductor depend sensitivity on the grain growth temperature. Researches for applications of high-T@sub c@. BPSCCO superconductor particles have been made to overcome the weak-link problem around the grain boundaries for higher J@sub c@. Shock compaction for BPSCCO superconductor particles have been investigated by shock compaction technique. After the shock compaction characterizations of as-shocked BPSCCO superconductor particles are investigated by X-ray diffraction(XRD)-analysis for the measurements of lattice parameters and SQUID-measurements for the susceptibility. The grain growth with growth steps of as-shocked BPSCCO superconductor particles are observed by AFM(Atomic Force Microscope) and SEM(Scanning Electron microscopy). The particle size distribution was measured by a laser diffraction size analyzer, which employed laser diffraction and scattering methods. In this measurement, use was made of an isopropyl alcohol for dispersing the BPSCCO particles. The average particles is found to be about 4.2 µm. The specimens were pressed into pellets with 10 mm in diameter and around 1 mm in thickness. These pellets were tightly encased in stainless containers. Shock compaction experiments were carried out under the shock pressure of around 2-5 GPa by using a propellant gun-system. From XRD-analysis, it is found that Bi-2223 phase is appeared clearly after the shock compaction process under 2-5 GPa with Bi-2212 phase. The Amplitude Mode image shows the surface details better than the unfiltered Height Mode images for BPSCCO particles. Tapping AFM image of the surface and edges for annealed BPSCCO particles at 850 °C for 96 hr after shock compaction. It is found from the section analysis that the vertical distance around edge area varies from 86 to 478 nm. BPSCCO superconductors, the Bi-2223 structures of as-shocked BPSCCO probably have shock-induced defects by the shock compaction. The ΔM (the difference of susceptibility at 5 K obtained from the temperature dependency of field cooling and zero field cooling at 20 Oe) which is proportional to J@sub c@, is measured by SQUID magnetometer. As a result, from the measurements of the susceptibility by SQUID magnetometer, it is found from the susceptibility measurements as a function of temperatures that ΔM clearly increases to 0.073 (emu/g) for as-shocked BPSCCO after annealed at 850°C for 48 hr,which seems to indicate the new pinning centers around the grain boundaries caused probably by the new defects of vacancies. The shocked specimens was compacted in platelet disk with a high crystal density over 97 %. The as-shocked specimen showed an oriented crystal structure with large grains of 3-5µm in length partly for shocked specimen by 2-5GPa. The ΔM (0.073 emu/g) of shocked specimen after annealing at 850° C for 48 hr became higher than that of starting specimen. These increase of ΔM indicate the introduction of a new pinning center through the shock compaction and annealing processes. The Amplitude Mode image of AFM show large edge effects which reflect the amplitude changes. Also form the section analysis of AFM, the vertical distance of 86-478 nm is obtained around the edge area in grains for annealed BPSCCO after shock compaction.

Surface Science
Room Exhibit Hall B - Session SS-TuP
Poster Session

SS-TuP1 HREELS and TPD Investigation of Electron Irradiation Effects on Diethylsilane-Covered Si(100) Surfaces at 100K*, **J. Lozano**, D. Early, J.H. Craig, Jr., P. Wang, K.R. Kimberlin,* Bradley University

The effects of 600-eV electron irradiation of diethylsilane (DES) adsorbed on Si(100) was studied using high-resolution electron energy loss spectroscopy (HREELS) and temperature programmed desorption. The effects of electron irradiation at submonolayer and multilayer DES coverages will be discussed. Previous electron stimulated desorption and TPD studies suggested an electron-induced beta hydride elimination process as a pathway for ethyl group desorption at 100K. The results of HREELS experiments performed to probe such processes will be discussed.

SS-TuP2 FTIR and XPS Studies of Porphyrin Containing Monolayers on Si(100) Surfaces*, **D.A. Syomin**, A.A. Yassery, F. Zaera, D.F. Bocian,* University of California Riverside

A number of mono-coordinated monolayers of redox-active Zn-containing porphyrins with a variety of organic linkers were prepared by thermal assembly onto hydrogen-terminated Si(100) surfaces. The porphyrin monolayers were characterized using attenuated total reflection (ATR) infrared and X-ray photoelectron spectroscopy (XPS) as well as standard electrochemical methods. The molecular orientation of the adsorbates within the monolayer films as a function of molecular coverage and type of organic linker used was investigated.

SS-TuP3 STM Study of Phosphine Adsorption on Si(111)-7x7 Surfaces*, **J.-Y. Ji**, T.-C. Shen,* Utah State University

PH@sub 3@ reaction with Si(111) surfaces has been studied by Yates et al. and Avouris et al. using a number of analytical techniques including UPS, AES, EELS and ESD in 1990. They concluded that PH@sub 3@ adsorbs dissociatively at 100 K and the surface is chemically inert. We are interested to revisit this system because the P-delta layer in the (111) direction may have interesting technological implications. In this report we present real space images of the PH@sub 3@ adsorption on Si(111)-7x7 at room temperature for various exposures between 0.3-60 L. Applying different sample biases we identify reacted and unreacted adatom sites. Similar to the ammonia adsorption, we find that center adatoms are more reactive than corner adatoms. However, careful analysis shows three different types of reacted sites which can be considered as PH@sub 3@, PH@sub 2@, and H adsorption sites. The coverage counting of the species suggests that most of PH@sub 3@ is dissociatively adsorbed on the surface at initial exposure generating H and PH@sub 2@ adsorption sites, followed by molecular adsorption of PH@sub 3@. Issues involving dissociation and desorption stimulated by electrons, saturation coverage at different substrate temperatures, and surface structures after annealing will be discussed. This work is supported by DARPA-QuIST program under ARO contract DAAD 19-01-1-0324.

SS-TuP5 Irradiation Effects of Undulator Synchrotron Radiation Beam on Hydrogen-Terminated Si (111) Surfaces Studied by STM*, **Y. Nonogaki**, T. Urisu,* Institute for Molecular Science, Japan

Undulator synchrotron radiation (USR) is a powerful light source for observation of surface VUV-photochemical reactions, since it is quasi-monochromatic and has high photon flux. It is also very attractive for semiconductor device processes using photochemical reaction. We have designed and constructed a beamline for surface photochemistry and nanofabrication of semiconductor at the UVSOR facility. Using this beamline hydrogen desorption on hydrogen-terminated Si (111) surfaces (H-Si (111)) was investigated using the USR and STM observation. We successfully observed that H-Si (111) was drastically changed after the USR irradiation. H-Si (111) was prepared with atomic H exposure to Si (111) 7x7 at surface temperature of 350°C for 10 min. The H-Si (111) was exposed to the USR at room temperature for 5 to 60 sec, where 1st harmonic of the USR was centered at 100 eV. Correspondent irradiation dose is 1000 to 10000 mAsec (ring current x time). STM observation was performed with tungsten tips at room temperature. STM observation of H-Si (111) showed that there were adatom islands and small protrusions on rest-atom monohydride surface. The adatom islands have triangular shape and bilayer height typically, of which coverage was ~15%ML. On the rest-atom monohydride surface, extension of unfaulted regions were observed and faulted regions was ~20%ML. Surface morphology was changed after USR irradiation. Density of the small protrusions significantly increased with irradiation dose from 1.4%ML at 0 mAsec to 12.8%ML at 10000 mAsec. The distribution of small protrusions were random whether on unfaulted and faulted region. The rest-atom monohydride surface seems to be unchanged. The small protrusions are assigned to dangling bond formed by irradiation-stimulated H-desorption from the rest-atom monohydride on the surface.

SS-TuP6 Theoretical and Experimental Comparison Studies of the Electronic Structure of Molecular Carborane Films*, **S. Balaz**, L.G. Rosa, A.N. Caruso, J.I. Brand,* University of Nebraska-Lincoln*; Y.B. Losovyj,* Louisiana State University*; P.A. Dowben,* University of Nebraska-Lincoln

Semiconducting boron carbide represents a new class of semiconductoing materials with applications in neutron detection and radioactive decay calorimetry [1,2]. The key to making a good boron carbide semiconductor requires materials fabrication by chemical vapor deposition (usually with plasma, electron beam, or synchrotron radiation assisted decomposition of the molecular precursor). The properties of the semiconducting boron carbide appear to be intimately connected to the source compound used. There is no obvious reason why different isomers of the closo-carborane, dicarbadodecaborane C@sub 2@ B@sub 10@H@sub 12@, should result in such different semiconducting properties [2,3]. Utilizing the synchrotron photoemission, and exploiting photovoltaic charging as a test of the n-type and p-type semiconductor behavior [4], during the deposition process, is key to developing the necessary understanding. Theory suggests little difference in electronic structure but profound differences are observed in experiment. Theoretical calculations from semiempirical calculations of the isolated 1,2 closo-carborane (orthocarborane) and 1,7 closo-carborane (metacarborane) molecules indicate that these isoelectronic carboranes should be very similar in HOMO-LUMO gap (highest occupied - lowest unoccupied molecular orbital). These calculations predicted 10.97 eV for the orthocarborane and 10.87 eV for the metacarborane. Since the two carboranes differ only in the positions of the two included carbon atoms and theory predicted the electronic states to be so close, great similarity in chemical and physical behavior would be expected, but is not observed. @FootnoteText@ [1]Robertson et al.,JP APL 80(19): 3644-3646 (2002) [2]A. N. Caruso et al., Journal of Physics Condensed Matter 16, L139 (2004) [3]A. N. Caruso et al., APL 84, 1302 (2004) [4]J.E. Demuth et al., Phys. Rev. Lett. 56, 1408-1411 (1986)[5]A.P. Hitchcock et al. J. Phys. Chem. B 101, 3483 (1997) .

SS-TuP8 Scanning Tunneling Microscopy Study of GaCrN Grown by MBE*, **M.B. Haider**, H.A. Al-Brithen, R. Yang, C. Constantin, D. Ingram, A.R. Smith,* Ohio University

According to Sato et al., (Ga,Cr)N is expected to show ferromagnetism above room temperature if the bulk Cr@sub Ga@ concentration is above 2%.@footnote 1@ Although many (mainly bulk) techniques have been applied to study dilute magnetic nitride systems here we apply in situ STM to investigate issues of Cr incorporation, Cr diffusion/segregation, and the effects of growth parameters. Cr-doped GaN(000-1) has been grown using rf-plasma MBE on sapphire (0001) at Ts ~ 700°C. The Ga/N flux ratio has been varied from 65-100% with variable Cr/Ga flux ratio between 3-11% for GaCrN growth. Based on the Ga/N flux ratio, three growth regimes were found: N-rich, metal-rich, and Ga-rich. It was found that under all three conditions GaCrN surfaces are smoother even to atomistic level forming 3x3 reconstructions after the growth as revealed by RHEED and AFM. This is in contrast to Ga-polar GaMnN case, where N and metal-rich surfaces are not smooth and under Ga-rich conditions Mn droplets of micron size are formed due to the Ga bilayer which exists during Ga-rich GaN(0001) growth.@footnote 2@ Atomic scale STM images of Ga-rich GaN(000-1) covered with 0.05ML of Cr deposited at 700°C show 3x3 and 6x6 reconstructions indicating the presence of Cr atoms within the surface structure. STM images of GaN(000-1) with Cr deposition of 0.2ML and above show some linear features suggesting transition from Cr substitution to 2nd order phase nucleation at the surface. The 3x3 reconstructions have been observed upon exposure of GaN(000-1) 1x1 to Cr at room temperature by RHEED and STM. These STM images suggest that on GaCrN surface, at low Cr concentration, Cr occupies Ga position. Another interesting phenomenon of contrast reversal of 3x3 and 6x6 reconstructions has been observed by STM on 5% Cr doped GaN(000-1) surface, which depends on the tip condition. @FootnoteText@ @footnote 1@Sato et al. J. Superconduc, 16 (2003) 31@footnote 2@Haider et al. J. Appl. Phys., 93 (2003) 5274.

SS-TuP9 Spatial Persistence and Survival Probabilities for Fluctuating Interfaces*, **M. Constantin**, S. Das Sarma,* University of Maryland*; C. Dasgupta,* Indian Institute of Science, India

We report the results of numerical investigations of the steady-state (SS) and finite-initial-conditions (FIC) spatial persistence and survival probabilities for (1+1)-dimensional interfaces with dynamics governed by the nonlinear Kardar-Parisi-Zhang (KPZ) equation and the linear Edwards-Wilkinson (EW) equation with both white (uncorrelated) and colored (spatially correlated) noise. We study the effects of a finite sampling distance on the measured spatial persistence probability and show that both SS and FIC persistence probabilities exhibit simple scaling behavior as a function of the system size and the sampling distance. Analytical expressions for the exponents associated with the power-law decay of SS and FIC spatial persistence probabilities of the EW equation with power-law correlated noise are established and numerically verified.

SS-TuP10 Sublimation Behavior of SiO@sub 2@ from Low and High-Index Si Surfaces Studied by Atomic Force Microscopy*, **J.C. Moore**, A.A. Baski,* Virginia Commonwealth University

We have used atomic force microscopy (AFM) to investigate the sublimation behavior of 100-nm thick oxide layers on the low-index Si(001) and high-index Si(5 5 12) surfaces. During high vacuum anneals, we have observed the formation of holes that nucleate at defects and grow laterally with annealing time (1 to 4 min, 1150@degree@C to 1350@degree@C). The depth of these holes is ~200 nm, or approximately twice the thickness of the oxide film. This is consistent with the thermal decomposition of SiO@sub 2@, where Si is extracted from the bulk in equal ratio to SiO@sub 2@ in order to form volatile SiO. As expected, the lateral growth of these holes is linear with annealing time (2 @micron@/min for 1200@degree@C). Interestingly, it is possible to obtain hole diameter data vs. annealing time by performing sequential anneals in vacuum, and then observing by AFM the formation of rings correlated to each anneal cycle at the bottoms of the holes. With regard to shape, holes formed on Si(5 5 12) have smooth edges and are circular, while those on Si(001) typically are not as circular. For both surface orientations, the holes oftentimes incorporate pits (5 @micron@ dia, 500-700 nm depth) or vertical structures (1 @micron@ dia, 150 nm height) at their centers. The conditions resulting in such structures, as well as their formation mechanism, are now under investigation. @FootnoteText@ This work is supported by the National Science Foundation.

SS-TuP11 The Structure of the (111) Surface of Bismuth*, **J. Sun**,* University of New Hampshire*; H. Mönig, J. Wells, P. Hofmann,* University of Aarhus, Denmark*; K. Pohl,* University of New Hampshire

Bismuth is a group V semimetal with a very low density of states at the Fermi level. However, a small distortion of its rhombohedral (A7) bulk structure would give a cubic lattice, which should be a good metal. In view of this close relation between structure and electronic structure it is not surprising that the surfaces of Bi are very different from the bulk material. They are good, two-dimensional metals with an electronic structure governed by spin-orbit coupling@footnote 1-3@. The changes in the geometric structure which lead to these interesting properties are totally unknown. We have studied the surface structure of clean Bi(111) and the mean-square displacement of the surface atoms by low energy electron diffraction (LEED). Experimental and theoretical diffraction intensities are analyzed for sample temperatures of 140, 171, 218, 268 and 313K. The optimization of the structural and nonstructural parameters is carried out by minimizing a R-factor with the quadratic tensor model algorithm. This results in an excellent agreement between the experimental and calculated data and R-factors of less than 0.1 are obtained. Moreover, the short termination of the bulk on the surface is confirmed. The temperature-dependent relaxations of the first layer distances and the atomic vibrations in the surface region are discussed. @FootnoteText@ @footnote 1@S. Agergaard, C. S@phi@ndergaard, H. Li, M. B. Nielsen, S. V. Hoffmann, Z. Li and Ph. Hofmann, New Journal of Physics 3, 15.1 (2001)@footnote 2@Ch. R. Ast and H. Höchst, Phys. Rev. Lett. 87, 177602 (2001)@footnote 3@Yu. M. Koroteev, G. Bihlmayer, J. E. Gayone, E. V. Chulkov, S. Blügel, P. M. Echenique, and Ph. Hofmann, cond-mat/0404461 .

SS-TuP12 Tunable Lattice Parameter of Ultrathin Bismuth Film*, **J.T. Sadowski**, Y. Fujikawa, T. Nagao, A. Al-Mahboob, T. Sakurai,* Tohoku University, Japan

The study of the structure and electronic properties of ultra-thin metal films on semiconductor surfaces has always attracted significant attention. To establish better control of the crystalline and electronic properties of the metallic layers, it is necessary to understand the factors governing their epitaxial growth, namely, surface free energies and stress relaxation effects. Semimetal bismuth (Bi) has distinctive electronic properties due to its covalent-like bonds and highly anisotropic Fermi surface. Moreover, results of our electron diffraction and scanning tunneling microscopy (STM) experiments show that Bi undergoes an allotropic transformation as a function of thickness on the scale of several layers, during the RT growth on Si(111)-7x7. After the initial formation of the Bi wetting layer, Bi grows with a new {012}-oriented phase, with a structure different from bulk Bi. With increasing the Bi coverage, above the critical thickness the film transforms into the bulk-like Bi(001) phase. Calculations suggest that the {012} phase with even-number layers is stabilized by forming a puckered-layer structure, which results in the formation of flat and well ordered film, reflecting the 2D structure of the {012} phase. Most interestingly, the lattice parameter of the Bi{012} phase can be tuned to a great extent by changing the nature and strength of the interactions between the Bi film and the substrate. Using the results of systematic diffraction and STM studies combined with the theoretical calculations, we will discuss the atomic structure of the Bi{012} film grown on the various surfaces (clean Si(111), H-Si(111), Bi and Au superstructures on Si(111)).

SS-TuP13 Stacking Fault Formation on Ir(111)*, C. Busse,* RWTH Aachen, Germany, Denmark*; C. Polop, T. Michely,* RWTH Aachen, Germany

The formation of stacking faults during homoepitaxial growth was observed in the model system Ir/Ir(111) (crystal structure: face-centered cubic) under a wide range of deposition parameters (sample temperature and deposition rate) using scanning tunneling microscopy (STM). A quantitative model can explain the observations and proves that stacking faults form out of small clusters that can occupy faulted hexagonal close-packed adsorption sites with significant probability in thermal equilibrium. Metastable areas in the wrong stacking sequence then grow out of these clusters by sufficiently fast addition of adatoms. This model is expected to hold for other systems as well. Upon further growth, islands in the same stacking coalesce, but islands in different stacking sequences do not. In the latter case, atoms can, however, move to the energetically favourable, regular stacking via a kink-flip process (self-healing). In the ideal case this leads to a complete disappearance of the wrong stacking and a defect-free film evolves. This effect can be observed in situ by annealing experiments.

SS-TuP14 Observation of Standing Waves in Si(111)@sr@3x@sr@3-Ag Islands at Room Temperature*, T. Ishizuka,* *H. Hirayama,* Tokyo Institute of Technology, Japan

It is widely accepted that Si(111)@sr@3x@sr@3-Ag surface has S1 surface state with a free electron like dispersion. The free-electron like surface dispersion has been confirmed by observing standing wave patterns at the @sr@3x@sr@3-Ag domain boundaries in STM at 5K [1]. In this study, we demonstrated that the free-electron like @sr@3x@sr@3-Ag surfaces can be utilized as the template for the nano-sized quantum structure construction. We obtained nano-scale @sr@3x@sr@3-Ag islands by depositing sub monolayer Ag on the Si(111)7x7 substrate surfaces at 770K. The standing wave patterns of electrons confined in the nano-islands were observed by a STM-based dI/dV mapping at 70K and room temperature. In the dI/dV images, the standing wave patterns were observed in the inside of the @sr@3x@sr@3-Ag islands of the size below 20nm. We found that the patterns persisted even at room temperature in the islands of 10nm scale. Then, we calculated the standing wave patterns numerically by solving Schrodinger equation for some islands with complex shapes using Finite Element Method(FEM). The numerical results reproduced characteristics of the observed standing wave patterns successfully, though the coincidence was not perfect. Furthermore, we fabricated point defects on @sr@3x@sr@3 Ag island artificially by using STM tip, and observed the resultant change of standing wave pattern. These results indicated that the 10nm scale islands still worked as Quantum Wells(QWs) even at room temperature. The shape of the islands could be modified by the STM tip induced atom manipulation. The confined electronic states are numerically predictable. These are preliminary demonstrations of the artificial design and fabrication of nano-sized QWs workable at room temperature on the template of the @sr@3x@sr@3-Ag surfaces.[1]N.Sato and S.Takeda PRB.59.3.2035(1999).

SS-TuP15 Electronic Structure of KDP and DKDP Nonlinear Optical Crystals Studied by Soft X-Ray Absorption and Emission Spectroscopies*, S.O. Kucheyev,* *C.F. Bostedt, T. van Buuren, T.M. Willey, S.G. Demos, T.A. Land, A.V. Hamza, T.E. Felter, L.J. Terminello, A.J. Nelson,* Lawrence Livermore National Laboratory

The surface and bulk electronic structure of KD@sub 2x@H@sub 2(1-x)@PO@sub 4@ single crystals, so-called KDP (x = 0) and DKDP (x > 0), with a deuteration degree x of 0.0, 0.3, and 0.6, is studied by soft x-ray absorption near-edge structure (XANES) and x-ray emission (XES) spectroscopies. High-resolution O K-edge, P L@sub 2,3@-edge, and K L@sub 2,3@-edge XANES and XES spectra reveal that the element-specific partial density of states in the conduction and valence bands is essentially independent of deuteration x. Projected densities of states in the conduction band also appear to be essentially identical for tetragonal and orthorhombic phases, consistent with previous band structure calculations. A decrease in sample temperature from 300 to 77 K results in an ~0.4 eV shift in the valence band edge (probed by XES), with negligible changes to the conduction band edge (probed by XANES) as the material transforms from the tetragonal to orthorhombic phase. We assign XANES and XES peaks based on previous molecular orbital and band-structure calculations. Results also show that high-intensity x-ray irradiation results in material decomposition into water and KPO@sub 3@ cyclo- and polyphosphates.

SS-TuP16 Nanoparticle Diffusion on Desorbing Solids: The Role of Elementary Excitations in Buffer-Layer-Assisted Growth*, V.N. Antonov,* *J.S. Palmer, P.S. Waggoner, A.S. Bhatti, J.H. Weaver,* University of Illinois at Urbana-Champaign

Physical vapor deposition onto rare gas buffer layers leads to the spontaneous formation of clusters. During the thermal desorption of the buffer, these clusters diffuse and aggregate into larger structures, a process known as buffer-layer-assisted growth and desorption assisted coalescence. We studied the effect of buffer thickness and the rate of buffer desorption on the extent of this aggregation for Ag, Au, Cu, Pd, Co, and Ni particles on a solid Xe surface. On the basis of these experiments, results from Monte Carlo simulations and the existing theoretical models for cluster-cluster aggregation, we report the Arrhenius parameters for nanoparticle slip-diffusion. The effective activation energies range from 0.12 for small Ag clusters (few hundred atoms) to 0.60 eV for ramified Ni islands (millions of atoms), and the giant pre-exponential factors were found to differ by many orders of magnitude. Significantly, the pre-exponential factors follow a Meyer-Neldel type dependence on the corresponding effective activation energy, with a characteristic Meyer-Neldel energy of 6.9 meV. This energy is associated with the phononic excitations in solid Xe that are responsible for nanostructure mobility. This dependence should be a characteristic feature of nanoparticle diffusion.

SS-TuP17 Epitaxial Cu Nanowire Arrays Grown on H-Si(110) using Glancing Angle Deposition*, H. Alouach,* *G.J. Mankey,* The University of Alabama

We report the growth of epitaxial nanowire arrays using the technique of glancing angle deposition with substrate rotation. Epitaxial copper nanowire arrays were deposited on H-terminated Si(110) using electron beam evaporation. The nanowire arrays were characterized with x-ray diffraction, atomic force microscopy and scanning electron microscopy. Individual nanowires were confirmed to be single crystal by examination with transmission electron microscopy. The epitaxial growth involves twin formation with the epitaxial orientation relationships: Cu(111)//Si(110) with Cu[1-10]//Si[001] and Cu[-110]//Si[001]. As the angle of incidence is increased, the Cu grows as isolated columns with a spacing that increases as the angle of incidence is increased. However, the thickness limit for epitaxial growth is reduced as the angle of incidence is increased, and it is approximately 300 nm for a deposition angle of 75°. The X-ray rocking curves for samples deposited at increasing polar angles show steadily improving crystal orientation up to a deposition angle of about 35°. Beyond 65° deposition angle, the rocking curves show split diffraction peaks indicating that there are two distinct orientations. In addition, the split peaks have a much lower FWHM. The observed behavior will be explained based on arguments involving unidirectional diffusion arising from adatom parallel momentum. This work was supported by the NSF.

SS-TuP18 Modification of Surface Electronic Structure Due to Scattering from a Quasi-Periodic Potential in Ag/GaAs(110)*, D. Eom,* *C.-S. Jiang, H.-B. Yu, Q. Niu,* University of Texas at Austin*; P. Ebert,* Institut für Festkörperforschung, Germany*; C.-K. Shih,* University of Texas at Austin

An extensive study has been done on the metal films grown on the semiconductor substrates because of their practical and scientific issues. One interesting system is the silver film deposited on the GaAs(110) surface using the so-called two-step process: If Ag is deposited on GaAs (110) surface at low temperature (~77K) and subsequently annealed to room temperature, then it will form an atomically flat film. A detailed morphology, however, looks more like an array of two stripes, one is thick and one is thin, whose sequence is quasi-periodic. By using this model system, we explore the effect of quasi-periodic potential on the surface states of the silver film using a low-temperature scanning tunneling microscope (LT-STM) operated at 5.5 K. Spatially resolved tunneling spectra are analyzed in reciprocal space (i.e. Fourier space). We found that such a quasi-periodically modulated potential leads to a very complicated electronic structures. Unlike the periodic potential that leads to energy gaps in the well-defined Brillouin zone boundary, the quasi-periodic potential results in a hierarchical structure of gaps in the k-space. Detailed analysis combining theory and experiment will be presented.

SS-TuP19 Structure and Thermal Stability of Thin Fe Films on Al(001) Surfaces with Ti Interlayers@footnote 1@*, C.V. Ramana,* Montana State University-Bozeman*; B.-S. Choi,* Jeonju University, South Korea*; R.J. Smith,* Montana State University-Bozeman

Thermal effects and chemical reactions can induce complex changes in the electrical and magnetic properties of thin metal film device structures. Achieving stability of these structures at elevated temperatures is therefore important to operation, and becomes more difficult as the film thickness is reduced to the nanometer regime. In the present work we investigate the structure of Fe films grown on the Al(001) surface with extremely thin Ti interlayers at the interface. Using Rutherford backscattering and channeling (RBS/c), we identify the bcc structure of the Fe(001) film, with the [100] axis rotated 45° relative to the [100] axis of the Al(100) substrate, and an interplanar distance of 1.44Å. RBS/c and low-energy ion scattering (LEIS) were then used to evaluate the thermal stability of the interface. The resulting epitaxial structure is observed to be stable for temperatures up to ~200°C, at which point the diffusion of Al towards the surface begins. At ~400°C, the sample structure begins to disorder. @FootnoteText@ @footnote 1@Work Supported by NSF Grant DMR-0077534.

SS-TuP20 XPS and AFM Study of K Promoted Supported Au Nanoclusters*, Y. Yang,* University of Calfornia, Santa Barbara*; M.M. Sushchikh, **S.A. Sardar**, E.W. McFarland,* University of California, Santa Barbara

It has been observed in high pressure reactors that K can increase the activity for CO oxidization of Au nanoclusters formed in block copolymer micelles and deposited on titania supports. UHV in situ characterization shows that the surface species, K@sub 3@ N and carbonates are discomposed after heating the surface to 800 K in UHV. K remains on the surface, however, the XPS signal from Au disappears during the heating process. Surprisingly, repeat XPS following exposure of the surface to air shows an observable Au signal. The appearance/disappearance of the Au XPS signal is reproduced by cyclically exposing the sample to the air then re-heating to 800 K in UHV. Sputtering the surface heated in UHV recovers the Au XPS signal. A K-shell model is proposed to explain the data with the formation of a K@sub 2@ CO@sub 3@ overlayer on the Au cluster during heating in UHV. The concentration ratio between Au and K is approximately1:1.

SS-TuP22 Formation and Characterization of Au Coatings Deposited by Pulsed Laser Deposition on Alumina Particles for Low Temperature Oxidation of CO*, C.E. Allmond, M.C. Raphulu, **J.T. Calla**, R.J. Davis, J.M. Fitz-Gerald,* University of Virginia

Laser induced atomic flux processing affects a wide range of existing and emerging products used in aircraft, cutting tools, lithium-ion rechargeable batteries, superconductors, pharmaceutical drug formulations that employ micron to submicron sized particulate precursors in their manufacturing process. By attaching atomic to nano-sized clusters either in discrete or continuous form on the surface of the core particles, i.e. nano-functionalization of the particulate surface, materials and products with significantly enhanced properties can be obtained. In this paper we present an alternative use for these materials in the area of Au catalysis. Bulk gold is considered the least reactive metal in heterogeneous catalysis due to repulsion between the orbitals of the adsorbate and gold's filled d states. Gold's catalytic potential is not realized until it is present as supported nanoparticles. Supported gold nanoparticles are recognized as active catalysts for a variety of reactions, such as oxidation, epoxidation of propene, hydrogenation, water gas shift, and NO reduction. Despite intense effort, the underlying principles and the degree of their contribution to the activity of gold catalysts are currently debated. Although not conclusive, several factors have been proposed to explain the high activity of gold nanoparticles. These factors can be generalized into three classifications; metal particle size, metal oxidation state, and synergy between the metal particle and the support.

SS-TuP23 The Development of Pd and Ag Nanoparticles with Pulsed Laser Deposition*, **C.E. Allmond**, J.M. Howe, V.P. Oleshko, J.M. Fitz-Gerald,* University of Virginia

Small particles in the 1-100 nm range often exhibit significant properties that are promising for various practical applications, such as catalysis, electronics, imaging systems, etc. Therefore, it is important to develop preparation methods that are simple, effective and flexible in controlling particle size distributions. The development of novel materials has grown considerably with the introduction of nanoscale processing. A wide range of synthetic approaches regarding the preparation of metal nanoparticles in various matrices and at the surfaces, including reduction, sol-gel precipitation, solvent evaporation of hydrophobic colloids, cross-linking in colloidal aggregates, templates-directed methods, and biopolymer superstructures, has been reported. As an alternative, pulsed laser deposition is a novel preparation method. Palladium and silver nanoparticles, with sizes ranging from 1-10 nm, were deposited onto transmission electron microscope grids using pulsed laser deposition. Analysis of these nanoparticles incorporated high-resolution transmission electron microscopy, electron energy loss spectroscopy (EELS), and electron dispersion spectroscopy (EDS). The rationale behind this is two-fold: (1) is to obtain mean particle size and crystal structure as a function of fluence, gas pressure, and gas type and (2) is to establish parameters for site-specific catalysts.

SS-TuP24 Characterization of the Near-surface Structure, Composition and Surface Chemistry of Ultrathin Au Films on Pd{111}*, **T.G. Owens**, C.J. Baddeley, T.E. Jones,* University of St. Andrews, UK*; T.C.Q. Noakes, P. Bailey,* CCLRC Daresbury Laboratory, UK

There are many examples where bimetallic catalysts are known to outperform their monometallic counterparts. The synthesis of vinyl acetate monomer (VAM) from acetic acid and ethylene by Pd/Au catalysts is one such example exploited commercially by BP. In order to gain a fundamental understanding of the catalytic role of Au, we are interested in how the chemistry of Pd/Au bimetallic surfaces is influenced by surface structure and composition. Previous studies of the Pd{111}/Au system have reported that the first Au monolayer grows psuedomorphically on Pd{111} at 300 K while subsequent growth consists of films possessing a more Au-like structure, i.e. classic Stranski Krastanov growth. Medium Energy Ion Scattering (MEIS) has a unique ability to probe structure and composition of crystalline surfaces as a function of depth with monolayer resolution. In parallel with Scanning Tunnelling Microscopy (STM) measurements, we reveal that Au growth is more complex than previously assumed and identify an interfacial alloy structure with a quite different structure to either Au or Pd. In addition, we report the behaviour of ultrathin Au films as a function of pre-annealing treatment and we probe how the structure and composition of the near surface region is influenced by the adsorption of simple probe molecules.

SS-TuP25 Highly Stable Variable Temperature STM for Atomically and Time Resolved Imaging: The Dynamics of Self-Assembly at Surfaces*, **B. Diaconescu**, G. Nenchev, K. Pohl,* University of New Hampshire

Self-ordering growth of nanoarrays on strained interfaces is an attractive option for preparing highly ordered nano-templates of specific feature size densities. High-tech methods used for reducing of the feature sizes may thus be supplanted by this simple and elegant patterning technique. Reconstructed surfaces, e.g. Au(111) or Pt(111), and monolayer thick strained films, e.g. Ag or Cu on Ru(0001), exhibit well-ordered networks of misfit dislocations. These networks can serve as templates for the growth of mesoscopic-scale structures of large-scale order and size uniformity. The combination of interfacial stress and corrosion creates self-ordering arrays of unprecedented regularity. The great potential of this natural templating approach is that the feature sizes and densities are predicted to depend on the interfacial stress in these strained layers. We have the unique capability of being able to measure the resulting driving forces of self-assembly directly through time-resolved scanning tunneling microscopy. This enables us to determine the stability and elastic constants of 2D nano-templates@footnote 1@. For this purpose we designed and build a highly stable VT-STM@footnote 2@. It allows us to study the dynamics of self-assembly at strained metallic interfaces at the atomic scale in the temperature range 80-400K. An overview of the instrumental setup and it's performance will be given by variable temperature studies of self-organisation of nanostructures on Au(111) and Ag, and Cu films on Ru(0001) at different thicknesess. @FootnoteText@ @footnote 1@ K.Pohl et al. Nature 397,238 (1999)@footnote 2@ Supported by NSF-CAREER-DMR-0134933 and ACS-PRF-37999-G5.

SS-TuP26 Preparation and Chemical Oxidation Kinetics of Microcrystalline Tungsten Bronze Thin Films*, **E.B. Kadossov**, P. Rajasekar, N.F. Materer,* Oklahoma State University

Microcrystalline tungsten bronze (H@sub x@WO@sub 3@) 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 photoelectron and ultra-violet photoelectron spectroscopy show that these films are indistinguishable from conventionally prepared tungsten bronze powders. 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 oxygen gas or hydrogen peroxide aqueous solution. The resulting decay of the 900 nm absorbance intensity with time can be satisfactory fit to a kinetic model composed of two elementary steps. First, a proton must diffuse from the bulk to the surface. Next, a chemical reaction between the surface proton and the oxidant must occur. Conditions are such that the surface concentration of the oxidant adsorbed on the surface is effectively constant. In addition, this model implicitly assumes that the electron transfer step required for reduction of the oxidant is not rate limiting. From this kinetic model, both the proton diffusion coefficient and the surface activation energies can be estimated. The results are compared with previous nuclear magnetic resonances studies and electrochemical measurements.

SS-TuP27 Growth Studies of Thin Pt Films on the Cu(100) Surface by CAICISS, LEED and XPS*, **M. Walker**, C.R. Parkinson,* University of Warwick, UK*; C.F. McConville,* University of Warwick, UK, United Kingdom

The formation of a surface alloy upon room temperature deposition of Pt on the Cu(100) surface is observed by co-axial impact collission ion scattering spectrscopy (CAICISS), low energy electron diffraction (LEED) and X-ray photoelectron spectroscopy (XPS). Simulations of the CAICISS results are given to support the proposed alloy structures from Pt coverages of 0.25 ML upwards, with comparisons between layer-by-layer, alloy and Pt surface cluster models. With increasing Pt coverage the surface region becomes Pt rich, with a small Pt overlayer observed at a Pt coverage of 2.35 ML and above. This indicates the onset of layer-by-layer growth of a pure Pt film. LEED observations indicate that this film is disordered. The effects of annealing at temperatures up to 600 °C are also shown for samples with Pt coverages of 0.25 ML and 2.75 ML. CAICISS and XPS clearly demonstrate the penetration of Pt in to the Cu substrate upon annealing. For Pt coverages greater than 2.35 ML, annealing at 300 °C causes Pt to penetrate down to the fourth and fifth layers of the substrate, forming a CuPt surface layer and Cu@sub2@Pt sub-surface layers. For Pt coverages of ~ 0.25 ML, annealing at 200 °C resulted in a small amount of Pt migrating towards the bulk. After annealing at 300 °C the sample contained approximately 7% Pt in each of the top three layers of the sample and small Pt concentrations in the fourth and fifth layers. Annealing at 600 °C results in the onset of significant migration in to the substrate in both cases.

SS-TuP28 NO Decomposition over K-Deposited Pd(111)*, **I. Nakamura**, H. Hamada, T. Fujitani,* National Institute of Advanced Industrial Science and Technology (AIST), Japan

The adsorption and thermal reaction properties of NO on a K-deposited Pd(111) surface were investigated using infrared reflection absorption spectroscopy, X-ray photoelectron spectroscopy, and temperature-programmed desorption. For the K-deposited Pd(111) surface, two different NO adsorption sites were observed in addition to the Pd site. On the clean Pd(111) surface, the adsorption of NO was purely molecular and reversible, but on the K-deposited surface, the adsorbed NO decomposed to N@sub 2@ at two different temperatures, 530 and 610 K. The N@sub 2@ desorption at 530 K was due to the dissociation of NO, indicating that the NO dissociation sites were created on the Pd(111) surface by the deposition of K. On the other hand, the N@sub 2@ desorption at 610 K was due to the decomposition of NO@sub 2@, which was formed by the reaction of adsorbed NO with oxygen produced by NO dissociation. It was clearly shown that two active sites for the decomposition of NO to N@sub 2@ were newly created on the K-deposited Pd(111) surface.

SS-TuP31 Charge Exchange between Alkali Ions and Cerium Oxide Surfaces*, **G. Liu**, J. Yarmoff,* University of California, Riverside

CeO@sub 2@ has interesting catalytic properties, which are presumably the result of an electronic configuration that includes many valence electrons. Earlier, we showed that the probability for neutralization of low energy alkali ions scattered from metal surfaces is determined by resonant charge transfer (RCT) along the exit trajectory, and it depends on the local electrostatic potential (LEP) a few Å's above the scattering site.@footnote 1@ We also showed that RCT is effected by localized confined states in nanomaterials.@footnote 2@ The present work investigates the charge exchange between alkali ions and cerium oxide surfaces. The neutral fractions of 3 keV @super 23@Na@super +@ ions singly scattered from the Ce sites on CeO@sub 2@ single crystal surfaces were measured with time-of-flight spectroscopy. The angular dependence of the neutralization was found to be isotropic for CeO@sub 2@(111), while for CeO@sub 2@(100) the neutralization decreases for more grazing angles. The results from either surfaces cannot be explained by simple RCT theory, which predicts increased neutralization at grazing angles, and may therefore suggest that a new mechanism for charge transfer is operative with these materials. In order to ascertain the influence of the work function on ion neutralization, Cs and Br were deposited onto the CeO@sub 2@ surfaces to controllably decrease and increase the work function, respectively. Results for scattering from CeO@sub 2@(100) and CeO@sub 2@(111) will be compared and contrasted. @FootnoteText@ @footnote 1@C. B. Weare and J. A. Yarmoff, Surf. Sci. 348 (1996) 359.@footnote 2@G. F. Liu, Z. Sroubek and J. A. Yarmoff, Phys. Rev. Lett., in press. .

SS-TuP32 Inelastic Energy Losses and Ion Yields of Low Energy Ar@super +@ and Ne@super +@ from Transition Metals*, **A. Kutana**, K.P. Giapis,* California Institute of Technology

Inelastic losses and relative ion yields of 100-1300 eV Ar@super +@ and Ne@super +@ ions reflected off polycrystalline V, Nb, Ta, Zr, and Y surfaces were measured using a low energy scattering beamline apparatus. Use of a floating ICP source coupled to a small beam accelerator had overcome many problems pertinent to conventional sources in the sub-keV energy range and allowed measuring scattering energies with much greater precision. From the acquired energy spectra, peak positions of singly scattered ions were plotted versus the primary beam energy E@sub 0@ and compared with energies of totally elastic single collisions. For energies above 100 eV, the inelastic losses of singly scattered ions can be described by the power law E@sub 0@@super a@ with a<1. Scattering simulations based on the binary collision approximation with added local and nonlocal inelastic losses yielded the theoretical loss values that were related with the ones observed in experiment. For a given primary ion, the relative ion yields were generally found to vary insignificantly from one metal to another, except for the Ne@super +@-Y pair, where a much more efficient neutralization of Ne@super +@ was observed. Characteristic neutralization velocities were also estimated for the above projectile-target combinations.

SS-TuP33 Epitaxial Iron Oxide Growth on Vicinal Pt(111): Well-defined Defective Model Systems?*, **G. Ketteler**,* Lawrence Berkeley National Laboratory, University of California*; W. Ranke,* Fritz-Haber-Institute of the MPG, Germany

Heterogeneous catalysts consist often of metals in contact with oxides and the activity depends on the interaction between them. In addition, the defect structure of the surface is of high importance for the catalytic activity. The common electron-based surface science techniques allow the characterization of model catalyst surfaces with atomic precision. Studied model catalyst systems include single crystal surfaces, epitaxial compound films, or well-defined particles deposited on single-crystalline supports. However, real catalysts contain a defect structure which is difficult to model in a well-defined manner. In order to study the controlled introduction of defects into iron oxide model catalysts for the dehydrogenation of ethylbenzene to styrene, we have grown different iron oxide phases on a stepped Pt(9 11 11) single crystal surface and characterized the film structures by STM and high-resolution SPA-LEED measurements. The hope was that this may provide a way to introduce well-defined step defects into the epitaxially grown films. For coverages below 1 ML, FeO(111) films wet the vicinal Pt substrate. The step structure changes under formation of doubled and triplicated terrace widths and step heights. Further cycles of iron deposition and oxidation lead to a Stranski-Krastanov-type growth of Fe@sub 3@O@sub 4@(111) islands which initially are elongated along the edge direction. However, the morphology of a coalesced closed film is almost unaffected by the underlying substrate step morphology. High pressure oxidation of Fe@sub 3@O@sub 4@ films results in poorly defined Fe@sub 2@O@sub 3@(0001). Although FeO films grown on the vicinal Pt surface may serve as model systems for systematic studies of well-defined defective oxide surfaces, the catalytically more relevant Fe@sub 3@O@sub 4@ and Fe@sub 2@O@sub 3@ phases could not be obtained reproducibly with a well-defined defect structure.

SS-TuP34 Anomalous Diffusion Permeability of an Interphase Interface in Mo-Ni System Under High-Energy Electron Irradiation*, **G.G. Bondarenko,** M.M. Yakunkim, A.V. Artamonov,* Moscow Institute of Electronics and Mathematics (Technical University), Moscow, Russia*; S.P. Ostashkin,* Russian State University of Innovational Technologies and Management, Moscow, Russia

Some of the problems of the theory of transport in solids are anomalous atomic mobility and deviations from the equilibrium concentrations at an interphase interface caused by high-energy irradiation. The problem of anomalous mass transfer of components during long-term electron irradiation can be solved using information on phase diagrams. We study the Mo-Ni system during electron irradiation over the time it takes for stationary state to be achieved and compare the states obtained with equilibrium states. Samples in form of two-layer plates 0.05 (Mo) and 1.5 mm (Ni) in thickness were irradiated in a linear electron accelerator at energies of E = 2-8 MeV in steps of 2 MeV for the time it took for equilibrium structures to be formed. Irradiation was carried out in a special temperature-controlled chamber at 1000 K. The isothermal section of this system at E = 0 was preliminary obtained. Isothermal sections of the phase diagram at various values of E were constructed from the data of phase analysis. We found that the quasi-equilibrium irradiated diffusion zone at the interface is a nanoregion ~20 nm in size. The concentrations of components at the interphase interface significantly change during irradiation. As a result of electron irradiation, the maximum nickel content in the @delta@-phase increases by 12%, the nickel concentration in the molybdenum-based solid solution at the interface increases by a factor of almost four and is equal to ~10% at E = 8 MeV. Changes in the component concentrations at interphase interfaces can be described without applying thermodynamics by introducing the concept of the diffusion permeability of an interphase interface. Given the appearance of a phase diagram at various values of E, it is possible to calculate the diffusion permeability of the interface for all cases. This approach was used to account for the concentration deviations detected at the interphase interface during high-energy electron irradiation.

SS-TuP35 Structure Transformation of Palladium and Iridium Clusters on the W (110) Surfaces at Initial Stage*, **T.-Y. Fu,*** National Taiwan Normal University, Taiwan, ROC*; Y.-H. Wang,* National Taiwan Normal University, Taiwan, Taiwan R.O.C.*; T.T. Tsong,* Institute of Physics, Taiwan

The initial stages of cluster nucleation of Pd or Ir adatoms on W (110) surfaces and in the vicinity of surface steps are observed directly by a field ion microscope (FIM). At the beginning, the most stable structures of Pd and Ir clusters are both linear chains, which are parallel to the nearest-neighbor stacking directions of the substrate. Different to the Pd clusters which the preferred structure is a 2-D compact island when the chain length is beyond 8 atoms, the linear Ir chains are apparently more stable and the greater coverage and higher temperature are necessary conditions for 1-D to 2-D transition. Both of Pd and Ir 2-D islands are pseudomorphic structure. As the number of Pd adatoms increasing to approximate monolayer coverage, the structures of clusters transfer to three-dimensional island. The structure transition from bcc (110) to fcc (111) of 3-D Pd clusters is shown. The quit complex transform behaviors of Ir clusters are also discussed.

SS-TuP36 Adsorption and Reaction of Oxygen and Hydrogen on Free Platinum Clusters*, **M. Andersson**, A. Rosen,* Chalmers University of Technology and Goteborg University, Sweden

In a cluster beam experiment metal clusters are produced with a pulsed laser vaporization source, kept at room temperature or liquid nitrogen temperature. The beam of neutral clusters passes two low-pressure collision cells and clusters and reaction products are detected with laser ionization and time-of-flight mass spectrometry. Thus, the reaction probability in a cluster-molecule collision can be determined.@footnote 1@ Stable reaction products with O@sub 2@ are detected for clusters with more than 6 atoms, and a high and relatively size-independent reaction probability of about 0.3 is measured. Also H@sub 2@ adsorbs readily on Pt@sub n@ but the exact number of adsorbed molecules is difficult to determine because of the Pt isotope distribution. If the clusters first react with O@sub 2@ and then with H@sub 2@ one can observe that the reaction of Pt@sub n@(O@sub 2@)@sub m@ with H@sub 2@ results in the removal of oxygen atoms from the cluster. This is interpreted as formation of water molecules, which subsequently desorb. The efficiency of the catalytic water formation is high on all cluster sizes measured (7-30 atoms), with only a weak dependence on cluster size.@footnote 2@ The configuration with two separate reaction cells enables reversing the order of interaction with the reactant molecules, and a high reaction efficiency is measured also when the Pt clusters first interact with H@sub 2@. @FootnoteText@ @footnote 1@ M. Andersson, J.L. Persson, and A. Rosen, J. Phys. Chem. 100, 12222 (1996).@footnote 2@ M. Andersson and A. Rosen, J. Chem. Phys. 117, 7051 (2002). .

SS-TuP37 Preperation of Ultra-thin Lattice Matched Multilayers of Cr@sub 0.63@Mo@sub0.37@ and MgO*, K.B. Gylfason,* Biopharmaceuticals, Iceland*; S. Olafsson, I. Meyvantsson,* University of Iceland, Iceland*; K. Johnsen,* Biopharmaceuticals, Iceland*; **J.T. Gudmundsson,*** University of Iceland, Iceland

We report on the preparation of a lattice matched hetheroepitaxial system in a magnetron sputtering discharge. Cr@sub 0.63@Mo@sub0.37@ thin films were grown on MgO(1 0 0) using a DC discharge, and an MgO overlayer was grown on top by reactive sputtering in a pulsed bipolar discharge. The composition of the binary metal alloy is chosen so that the film is lattice matched to the substrate when the direction of the film is parallel to the direction of the substrate. Ex situ X-ray diffraction (XRD) and low angle X-ray reflectivity measurements were performed to determine the film structure, film thickness, as well as the surface and interface roughness. The minimum thickness for continuity of the binary metal alloy film was determined using four point probe resistance measurements. The insulating properties of the MgO film as a function of thickness were assessed by measuring the tunnelling current I-V characteristics of a metal-insulator-metal structure.

SS-TuP39 O2-covered Reduced TiO2(110) Rutile: Dynamics and Chemistry*, **Y. Wang**, G.S. Hwang,* The University of Texas at Austin

The rutile TiO2(110) surface has been widely used as a catalyst for photochemical reactions and a support for transition metal catalysts. Molecular O2 adsorption plays an important role in determining the activity of TiO2 and supported metal catalysts. Surface bound oxygen species may directly influence chemical and photochemical processes occurring on TiO2. In addition, O2 exposure leads to significant structural changes of supported metal particles, which may in turn affect their catalytic activity. It has been found that molecular O2 adsorbs on TiO2(110) only when O-vacancies are present. Despite its importance, however the exact chemistry and dynamics of adsorbed O2 molecules on reduced TiO2(110) are still unclear. Using density functional theory calculations, we have investigated the adsorption and diffusion of oxygen species on the reduced TiO2 (110) surface. We have found that molecular O2 strongly binds not only to O-vacancies, but also to Ti(5c) neighbors, due to delocalization of unpaired electrons arising from removal of neutral bridging oxygen. Our results show that molecular O2 can jump across an oxygen vacancy and diffuse along a Ti(5c) row with moderate barriers. On the other hand, atomic O diffusion along a Ti(5c) row is rather unlikely at low temperatures (< 300K), because of the relatively higher probability of O-O formation by interaction with an adjacent bridging O(2c) atom. Based on our calculation results, we will discuss the diffusion and healing of O vacancies associated with O2 adsorption. We will also present the structure and energetics of higher coverage O2 adsorption and the chemistry of O2-covered reduced TiO2(110) surfaces.

SS-TuP40 Growth and Reactivity of Pt, Rh and Pt-Rh Nanoparticles on TiO@sub 2@(110)*, **S. Ma**, J.S. Ratliff, D.A. Chen,* University of South Carolina

Pt, Rh and Pt-Rh nanoparticles have been deposited on TiO@sub 2@(110) at room temperature and have been characterized by scanning tunneling microscopy (STM). The deposition of a small amount of Pt on the surface (0.12 ML) results in particles with an average diameter of 22.7+4.2 Å and height of 4.4+1.2 Å. In contrast to the growth of Cu and Ni on TiO@sub 2@(110), the Pt particles do not exhibit a preference to reside at the step edges. At higher Pt coverages (2 ML), the average size of the particles increases to 30.4+4.6 Å in diameter and 8.5+2.0 Å in height. Larger particles with roughly the same size distribution could be produced by depositing at room temperature and annealing to elevated temperatures. For example, after annealing the 2 ML coverage of Pt to 500 K, particles sizes ranged from 40-45 Å in diameter and ~10 Å in height. Further heating to 700 K increased the sizes of the particles to ~50 Å in diameter and 10-12 Å in height, and the largest particles were prepared by annealing at 1000 K (60 Å in diameter, 15 Å in height). Since Pt particles on TiO@sub 2@ are known to encapsulate with a TiO@sub x@ species upon annealing, X-ray photoelectron studies were carried out on the Pt particles annealed to 1000 K. However, there was no evidence for Ti@super +4@ reduction or Pt oxidation in the Ti(2p) and Pt(4f) regions. Possible encapsulation of the nanoparticles by TiO@sub x@ will be further studied by low energy ion scattering as well as grazing angle X-ray photoelectron spectroscopy experiments. The reduction of NO by CO on the monometallic and bimetallic clusters of different sizes will be investigated by temperature programmed desorption.

SS-TuP41 Adsorption of L-phenylglycine on Anatase TiO@sub2@(101) and (001): A NEXAFS and Photoemission Study, ***A.G. Thomas,*** University of Manchester, UK, U.K.; *C. Chatwin, W.R. Flavell, D. Tsoutsou,* University of Manchester, UK; *T. Johal, J. Purton,* CCLRC Daresbury Laboratory, UK

We present a study of the adsorption of L-phenylglycine from submonolayer to multilayer coverage on the (101)(1x1) surface of anatase phase TiO@sub2@. Photoemission is used to determine changes to the electronic structure of the substrate and adsorbate and the NEXAFS searchlight effect is used to determine the orientation of the phenylglycine on the substrate. NEXAFS spectra recorded from multilayers adsorbed from the vacuum show good agreement with solvent deposited thick films of glycine and phenylalanine@footnote 1@. From the intensity dependence of the ring @pi@* resonance on photon incidence angle in NEXAFS it appears that the molecule forms a disordered layer at all coverages studied here. Furthermore, again at all coverages studied, it appears that N is being lost from the amino acid molecule with time through a photon induced process. A similar result has been observed when glycine adsorbed on the rutile TiO@sub2@ (110)(1x2) surface is subjected to photons of energy 55 eV@footnote 2@. @FootnoteText@ @footnote 1@ J. Boese, A. Osanna, C. Jacobsen, J.Kirz. J. Electron Spectroscopy and Relat. Phenom. 85 (1997) 9.@footnote 2@ E. Soria, I. Colera, E. Roman, E.M. Williams, J.L. De Segovia. Surface Science 451 (2000) 188.

SS-TuP42 Deconvolution of the Fuchs-Kliewer Phonon Spectrum of Co@sub 3@O@sub 4@(110) Single Crystal Surfaces, ***E.M. Malone,*** *S.C. Petitto, M.A. Langell,* University of Nebraska-Lincoln

The Fuchs-Kliewer phonon spectrum of single crystal Co@sub 3@O@sub 4@(110) has been treated with a Fourier transform log deconvolution method which removes multiple scattering features from the single loss spectrum. Auger electron spectroscopy (AES), X-ray photoelectron spectroscopy (XPS) and low-energy electron diffraction (LEED) first characterized the Co@sub 3@O@sub 4@ crystal establishing the cleanliness, composition, and order of the (110) surface. High resolution electron energy loss spectroscopy (HREELS) was then used to obtain the phonon spectrum over the incident electron energy range of 2.25 to 14.25 eV. Due to the strong dipole cross section for the Fuchs-Kliewer phonon modes, intense multiple electron scattering was detected, which provided a complicated and overlapping combination of all possible loss modes. Deconvolution removed the multiple loss modes to produce well-resolved Fuchs-Kliewer fundamental phonon losses at 26.8, 47.5, 71.1 and 84.7 meV (216, 383, 573 and 683 cm-1). The series of multiple loss peaks were also identified using standard peak fitting procedures, which also confirmed the single loss energies obtained with the deconvolution procedure.

SS-TuP43 Kinetic Energy Dependent Oxidation Processes on Copper Surfaces, ***K. Moritani,*** Japan Atomic Energy Research Institute, Japan; *M. Okada,* Osaka University, Japan; *A. Yoshigoe, Y. Teraoka,* Japan Atomic Energy Research Institute, 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, for example, high Tc superconductors of cuprates and solar cells. Thus, many experimental and theoretical studies have been performed to understand the oxidation of Cu. However, the oxide-formation processes have been little elucidated from kinetics and dynamics points of view. In the present work, we studied the oxidation of Cu surfaces with a hyperthermal O@sub 2@ molecular beam (HOMB) using 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. The incident direction of the HOMB is along the surface normal of the sample. The surface temperature was kept at 300 K. After the irradiation of a proper amount of HOMB, high-resolution XPS spectra were measured at ~300 K using SR. We measured O-uptake curves, determined from the integration of O-1s XPS on the Cu(111), (100) and (110) surfaces spectra, after the HOMB irradiation and the exposure to the oxygen atmosphere. The kinetic energy of HOMB varied from 0.1 to 2.3 eV. The oxidation under 0.3 ML on the Cu(111) proceeded efficiently even with the ambient thermal O@sub 2@ gas, while further oxidation required the higher kinetic energy of O@sub 2@ molecules. The oxide structure above 0.3 ML changed to be a distorted Cu(100)-(@sr@2X@sr@2)R45°-O layer on the Cu(111). This reconstruction is induced by the additional incident energy. We will compare the data on Cu(111), (100) and (110) surfaces and discuss possible models of oxidation processes of Cu on the basis of the incident-energy dependence of the O-uptake curve.

SS-TuP44 The Adsorption of Benzene on Oxide Surfaces, ***M.-S. Chen,*** *A.K. Santra, D.W. Goodman,* Texas A&M University

The orientation and growth of benzene on various well-ordered oxide surfaces have been investigated with high resolution electron energy loss spectroscopy (HREELS), Auger spectroscopy (AES) and low-energy electron diffraction (LEED). Benzene on the Mo(112)-c(2x2)-[SiO4] surface is bound with its molecular plane parallel to the surface plane at submonolayer coverages. At intermediate coverages (1-3 ML), in contrast to benzene adsorption on metal surfaces, a layer-by-layer growth model where the benzene molecules bond parallel to the surface is observed. This is the first reported observation of benzene multilayer growth where the benzene molecules remain exclusively in a configuration parallel to the surface plane. In contrast, on SiO2 and TiOx thin films grown on the Mo(112), a tilted adsorption geometry with layer-by-layer grew up to 5-6 ML was found with a crystalline phase occurring at higher coverages. On a TiOx-SiO2 surface, where both parallel and tilted-up geometries coexist, crystalline benzene clusters formed at the second layer.

SS-TuP45 Competing Kinetic and Energetic Effects in the Adsorption of Ortho- and Para-H@sub 2@ on NaCl(001), *J.P. Toennies,* Max-Planck-Institute für Strömungsforschung, Germany; ***F. Traeger,*** Ruhr-Universität Bochum and MPISF Göttingen, Germany; *C. Wöll,* Ruhr-Universität Bochum, Germany

Due to the electrostatic interaction of the hydrogen molecule's quadrupole moment with the electric field of the surface the ortho and para modifications experience slightly different molecule-surface potentials, which has been verified by scattering of n- and p-H@sub 2@ beams from the clean NaCl surface. A complementary way to study the molecule-surface interaction is to investigate the (1x1) monolayers of n-H@sub 2@ and p-H@sub 2@ on NaCl at 8 K with elastic and inelastic He atom scattering. The ortho-para differences result in 10-12 % higher frequencies for the external vibrations of o-H@sub 2@. Therefore, the relative intensities of the peaks in time-of-flight spectra of the scattered He atom provide information on the composition of the layer. Under steady-state conditions at H@sub 2@ gas pressures between 2.5 x 10@super -8@ mbar and 9.3 x 10@super -7@ mbar as well as during the desorption of the layer without gas pressure time-of-flight spectra have been recorded and are compared to desorption curves, i.e. the specular He intensity during desorption. Conflicting evidence regarding the adsorption probability for ortho- and para-H@sub 2@ is found, which is only partly in agreement with a model of thermodynamically and kinetically controlled adsorption proposed by Heidberg et al. from IR spectroscopy.

SS-TuP46 First Stages of Water Absorption on Alkali Halides Surfaces Studied by Scanning Polarization Force Microscopy, ***A. Verdaguer,*** *G.M. Sacha, M. Salmeron,* Lawrence Berkeley National Laboratory

Adsorption of water on sodium chlorite has been studied using scanning polarization force microscopy. A crystal is cleaved at low humidity (10% RH) and then humidity is increased as topography, contact potential and mobility of the ions is measured. At a critical humidity (40% for NaCl) important changes in the surface potential and ionic mobility occurred. Topographical changes occurred as well, in the form of step motion. We focused our study on the changes on the surface immediately before this critical humidity is reached. The evolution in the topographical and electrical properties and the ion mobility on the steps and the terraces as we approach to that point has been studied. An increase in the topographic contrast on the steps appears as we approach to the critical humidity. The increase in topographic electrostatic contrast is due to an increase in ionic mobility at step, indicative of ionic dissolution. As the mobility increases the difference between the local potential at the steps and on the terraces, measured from the Kelvin Probe signal, decreases. This supports the model deduced from the topography and indicates that the initial potential at the steps disappears due to the increased ionic mobility. The data obtained suggest us a model for the first stages of the dissolution of the crystal.

SS-TuP47 XPS and XAS Study of Water and Atomic Oxygen Co-absorbed on Pt(111), ***L.-A. Naslund,*** *K. Andersson, T. Schiros,* Stockholm University, Sweden; *H. Ogasawara, A. Nilsson,* Stanford Synchrotron Radiation Laboratory

The chemical interaction between water and a metal surface is important in many practical fields, including corrosion, electrochemistry, molecular environmental science and heterogeneous catalysis. On hexagonal metal surfaces, like Pt(111), water molecules adsorb intact with strong intermolecular forces between the water molecules. A combined X-ray photoemission spectroscopy (XPS) and x-ray absorption spectroscopy (XAS) study shows that water (D@sub 2@O) co-adsorbed with atomic oxygen on Pt(111) stimulate dissociation of the water molecule and form a saturated hydrogen bonded network of OD and D@sub 2@O in the surface plane. The interaction with the Pt(111) surface is strong and give rise to a chemical shift of the Pt 4f orbital that is different from the results for water on Pt(111). XAS with polarized light shows that OD is standing up while D@sub 2@O is laying down. The amount of OD and D@sub 2@O are 0.28 ML and 0.55 ML, respectively, which gives an OD/D@sub 2@O ratio of 2. Upon heating D@sub 2@O desorbs and a reversible process gives back atomic oxygen.

SS-TuP48 XPS Study of Water on Cu(110)*, K. Andersson, A. Gomez,* Stockholm University, Sweden*; C. Glover,* MAXLab Lund University, Sweden*; L.G.M. Pettersson,* Stockholm University, Sweden*; **A. Nilsson**, H. Ogasawara,* Stanford University

The chemical interaction between water and a metal surface is important in many practical fields,including corrosion, electrochemistry, molecular environmental science and heterogeneous catalysis. On smooth metal surfaces, (e.g. fcc(111)), water molecules adsorb intact with strong intermolecular forces between the water molecules. This leads to the formation of a hexagonal two-dimensional ice lattice proposed as a "bilayer structure". The unit cell contains two water molecules, which are different in the interaction with respect to the metal surface. On the other hand, less is known about the behaviour of water on atomically rough surfaces (e.g. fcc(110)). An x-ray photoelectron spectroscopic (XPS) study was undertaken of the water/Cu(110)-system and we find that water adsorbs non-dissociatively on Cu(110) at temperatures below 165 K in contrast to a previous XPS study@footnote 1@. Above 165 K we find partial dissociation to take place. @FootnoteText@ @footnote 1@ Ch. Ammon, A. Bayer, H.-P. Steinruck and G. Held, Chem. Phys. Lett. 377 (2003) 163â?"169.

SS-TuP49 Water Dissociation on Ru(001): An Activated Process*, **H. Ogasawara**,* Stanford Synchrotron Radiation Laboratory*; K. Andersson,* Stanford Synchrotron Radiation Laboratory, Stockholm University, Sweden*; T. Schiros,* Stockholm University, Sweden*; A. Nikitin,* Stanford University*; L.G.M. Pettersson,* Stockholm University, Sweden*; A. Nilsson,* Stanford Synchrotron Radiation Laboratory

The chemical interaction between water and a metal surface is important in many practical fields, including corrosion, electrochemistry, molecular environmental science and heterogeneous catalysis. On Pt(111), it was shown that in the first layer all the molecules bind directly to the surface and to each other through the in-layer H-bonds without dissociation, creating a nearly flat overlayer. The water molecules are adsorbed through alternating metal-oxygen (M-O) and metal-hydrogen (M-HO) bonds@footnote 1@. On Ru(001), the water layer on Ru(001) shares similarities with the first water layer on Pt(111). We, however, obtained a dissociated state by irradiation of the adsorbed film by x-rays or heating the surface in water vapor above the desorption temperature. The latter shows a clear isotope effect between H20 and D2O indicating an activated dissociation process with a barrier slightly larger than the desorption channel. Previous theoretical and experimental disagreements can be explained in terms of electron or x-ray beam induced dissociation and under estimation of the dissociation barrier. We will also discuss about the bonding mechanism of water on Ru(001) based on DFT calculation. @FootnoteText@ @footnote 1@ H. Ogasawara et al, Phys. Rev. Lett. 89 (2002). .

SS-TuP50 Investigation of OH Desorption Energies and Reaction Paths within the H2/O2 Reaction on a Pd Catalyst using Kinetic Modelling and Laser-induced Fluorescence*, J.C.G. Andrae,* Royal Institute of Technology, Sweden*; A. Johansson,* Goteborg University and Chalmers, Sweden*; **P. Bjornbom**,* Royal Institute of Technology, Sweden*; A. Rosen,* Goteborg University and Chalmers, Sweden

A kinetic model for the H@sub 2@/O@sub 2@ reaction on a polycrystalline palladium catalyst has been constructed from experimental data. The aim was to obtain a deeper understand of the coverage-dependent OH desorption energy. The CHEMKIN software package was used in the modelling and each adsorbed oxygen atom was set to cover four Pd surface sites. The yield of OH and the water production were measured with laser-induced fluorescence (LIF) and microcalorimetry as a function of the relative hydrogen concentration, @alpha@@sub H2@. The temperature of the catalyst was 1300 K, the total pressure was 13 Pa and the flow was set to 100 SCCM. In fitting the model to the experimental data, the OH desorption energy E@super d@@sub OH@ was found to have a first-order coverage dependence according to: E@super d@@sub OH@ (@theta@)= E@super d@@sub OH@(0)-B@theta@, where @theta@ is the total coverage and B is a constant set to 92 kJ/mol. The desorption energy at zero coverage E@super d@@sub OH@(0) was determined to be 226 kJ/mol. The model could qualitatively and quantitatively reproduce the OH apparent desorption energy as a function of @alpha@@sub H2@ therefore it is believed that the coverage could be predicted by the model. It was found that the coverage on the Pd surface is in principle dominated by oxygen for all @alpha@@sub H2@. The values for E@super d@@sub OH@ (@theta@) were calculated as a function of @alpha@@sub H2@. Results of sensitivity analysis and rate of production calculations using this model imply that the main water-forming reaction on Pd at 1300 K is the hydrogen addition reaction H+OH ->H@sub 2@O.

SS-TuP51 What Can We Learn from Core Level Spectroscopy Studies of Ice?*, **D. Nordlund**,* Stockholm University, Sweden*; H. Ogasawara,* Stanford Synchrotron Radiation Laboratory*; M. Odelius, M. Cavalleri,* Stockholm University, Sweden*; P. Wernet,* BESSY, Sweden*; M. Nagasono,* Kyoto University, Japan*; B. Brena, M. Nyberg, L.G.M. Pettersson,* Stockholm University, Sweden*; A. Nilsson,* Stanford Synchrotron Radiation Laboratory

Core level spectroscopy is a powerful tool to obtain information on the unoccupied and occupied valence electron structure. The sensitivity of the valence electronic structure of water to different local H-bond situations is presented, where ice is used as a model system to approach important scientific aspects such as the local structure of liquid water, nature of the hydrogen bond, radiation induced ultrafast dissociation of water, and electron delocalisation and trapping processes. A number of experiments are presented together with spectral calculations based on density functional theory, revealing important information on the above listed aspects.

SS-TuP52 Self-Organized Growth of Nanopucks on 2D Pb Quantum Islands*, **Y.P. Chiu**,* National Taiwan Normal University, Taiwan*; H.Y. Lin, L.W. Huang,* Academia Sinica, Taiwan*; C.S. Chang,* Academia Sinica, Taiwan, Taiwan, ROC*; T.T. Tsong,* Academia Sinica, Taiwan

Self-organized growth is an attractive approach where a large number of structures can be formed simultaneously. The drawback for this approach involves the apparent difficulty in control of the structureâ?Ts size, their chemical homogeneity, and spatial arrangement. Several routes were taken to search for suitable templates on which the self-organized growth could be made tangibly practical. Regular strain-relief dislocations, periodic surface reconstructions, and Morie patterns have all been applied in attempt to improve the quality of self-organized growth. In this work, we employ the superstructures (electronic MoirÃ¨ patterns) found on 2D lead (Pb) quantum islands as a template to further grow self-organized 2D clusters (nano-pucks) of various materials. These patterns, originating from charge redistribution in the island in response to the lattice-mismatch-induced interfacial potential variation, thus differ from structure-driven templates. The boundaries of the periodic pattern are apparently repulsive for adatom diffusion. The activation energies for defining the template strength in trapping surface atoms have been obtained, which provide the practical parameters for controlling the size and spatial distribution of the nanopucks. A bi-layer complementary alternating behavior, similar to the confinement-induced phenomenon found in Pb quantum islands, also occurs in the growth of Ag nanopucks on the Pb islands of various thicknesses.

Vacuum Technology
Room Exhibit Hall B - Session VT-TuP
Poster Session

VT-TuP1 Mathematic Simulation of Processes in Flow Parts of Hybrid Turbomolecular Vacuum Pumps*, **M.G. Sapeshinsky**,* Bauman Moscow State Technical University, Russia

Mathematical models of process of carry of molecules are developed the channel, allowing to optimize a flowing part hybrid turbomolecular the vacuum pump (TMP) in a wide range speeds. Interaction of steps and flowing is investigated parts turbomolecular the vacuum pump with various constructive schemes. The design procedure of parameters is developed TMP with axial-radial a stream of gas. The algorithm is developed optimization flowing part TMP with axial and axial-radial stream gas, laws of change of geometrical parameters are received on to steps of a compound flowing part. Theoretical researches were carried out with use of a method of statistical tests and a method of angular factors. Experimental researches were carried out in laboratory conditions on models and experimental samples. Algorithm of optimization at presence nonlinear functional restrictions on controlled parameters uses algorithm sliding the admission and a method of absolute penal functions under condition of maintenance set speed of action of the pump on the chosen gas, and also on several gases. The problem of optimization is put as variational. Therefore the absolute penalty function is used, if in current optimization step S@sub real@ will be less than S: F(x,@rho@) =@Phi@(x)+@rho@ |(S@sub real@ - S) < 0| , where @rho@- penalty parameter, the upper value of which is restricted by bad dependence F(x,@rho@). After calculation of evacuation characteristic at current values of controlled parameters it is possible the situation, when P is less, than the limit rest pressure P@sub min@. In this case the value S@sub real@ is taken 0, and the target function is formed as follows: F'(x, @rho@, @rho@ @sub 1@)=Φ(x)+@rho@ |(S@sub real@ - S) < 0 |+ @rho@ @sub 1@ |{(lg (P)- lg(P@sub min@)}< 0| , @rho@ is chosen equal 10@super 5@. Minimization of flow part volume of TMP with axial and, the more, with axial-radial gas flow with given technical conditions for nitrogen (N@sub 2@) does not guarantee the required operation rate for light gases (H@sub 2@, He) due to nonlinear character of dependence S@sub max@ of axial and axial-radial rotors on round velocity when U/V <1. Therefore, if, for example, it is needed to minimize the flow part's volume of a TMP with given evacuation rate S at P for nitrogen N@sub 2@ and given evacuation rate S at P for hydrogen H@sub 2@, the absolute penalty function is formed as follows: F''(x, @rho@, @rho@ @sub 1@ , @rho@ @sub 2@ , @rho@ @sub 3@)= Φ(x)+@rho@|(S@sub real@ - S) < 0|+ @rho@ @sub 1@|{lg(P)-lg(P@sub min@)} < 0|+ @rho@ @sub 2@ |(S@sub real@, H- S) < 0|+@rho@ @sub 3@ |{lg (P) - lg(P@sub min@, H)} <0| , where P@sub min@, H - limit rest pressure for H@sub 2@. Naturally, it is necessary to calculate the discrete evacuation characteristic for H@sub 2@.Often in technical conditions are included different restrictions on other outgoing and optimization parameters, e.g. rotation frequency f, external diameter D@sub 2@ etc.

VT-TuP2 Measurements of Photon Stimulated Desorption from a Copper Beam Chamber wall During Four Years of Synchrotron Radiation Exposure@footnote 1@*, **C.L. Foerster**, C. Lanni,* Brookhaven National Laboratory

Photon Stimulated Desorption (PSD) has been continuously measured from a copper beam chamber for more than four years. Vacuum surface oxide had been completely removed prior to the start of measurements in order to reduce the initial PSD. Desorption rates were found to decline uniformly during the long-term exposure. Measurements of PSD and specular photon reflection were performed on NSLS beamline U9a at Brookhaven National Laboratory. It is well known that PSD causes a pressure rise in accelerator and storage ring vacuum, which limits their commissioning and performance. A copper beam chamber from a previous experiment was chemically etched and chemically cleaned prior to installation on beamline U9a. Previous PSD measurements on other chambers have shown that this chemical treatment removes any memory of prior exposure or conditioning. After installation, the copper chamber and end stop were vacuum baked to 250°C for more than a week to completely remove vacuum surface oxides. The chamber was exposed to more than 3x10@super 25@ photons direct from the source having a critical energy of 595 eV and striking at an incident angle of 100 mrad. The major PSD yields for hydrogen, carbon monoxide, carbon dioxide, and methane are reported as a function of accumulated photon flux and preparation. The initial PSD yields for the copper chamber after oxide removal were greatly reduced compared to previous measurements at this laboratory and those reported from other laboratories. The PSD component gases remained the same during the long exposure and all were significantly reduced. Carbon dioxide and methane were reduced much more than hydrogen and carbon monoxide. Specular photon reflection did not change significantly during the extended exposure.@footnote 1@ Work performed under the auspices of the U.S. Department of Energy, under contract DE-AC02-98CH10886.

VT-TuP3 Continued Vacuum Pump Oil Testing at the National Synchrotron Light Source to Minimize Oil Waste@footnote 1@*, C.L. Foerster,* ***J.-P. Hu,*** *E. Haas,* Brookhaven National Laboratory

An oil-testing project was established to determine if synthetic vacuum pump oil could be used effectively to reduce the large amount 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 used at the NSLS facility, such that a longer oil change interval would greatly reduce maintenance costs as well as oil waste. Initial 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 of the same size two-stage mechanical pumps were set up and run simultaneously having the same gas load. Convectron gauges, cold cathode gauges, and isolation valves were connected to a central vacuum chamber having a common inlet pressure control and a sampling valve for residual gas analysis. To simulate oil degradation produced by long-term mechanical pump operation, the system air load was manually controlled, with an air bleed valve in a common vacuum chamber, which was periodically adjusted, to run the pumps at a 500 mTorr inlet pressure. Vacuum pump oil suppliers to expedite the oil viscosity change, acid buildup, and pump-wear debris production suggested the pressure for mechanical pump testing. At this inlet pressure, the testing time is reduced and any oil back streaming is minimized. After one 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.@footnote 1@ Work performed under the auspices of the U.S. Department of Energy, under contract DE-AC02-98CH10886.

VT-TuP4 Adsorption System Controlled with Surface Roughness for Smooth Sliding in a Vacuum*, **A. Kasahara**, M. Goto, Y. Pihosh, M. Tosa,* National Institute for Materials Science, Japan

Friction measurement was measured out on typical vacuum materials as Copper sheets and type 304 austenitic stainless steel sheets after such surface treatments as chemical polishing or electrochemical buffing. We have shown that the materials with surface roughness around 100nm can offer as smooth sliding in a vacuum as at an atmospheric pressure with a developed vacuum friction measurement system based on Bowden-Leben type system. This smooth sliding may arise from absorption gas layer as lubricant kept in hollows of surface nanoscopic asperities. We accordingly estimated adsorption gases for lubrication by decrease in sliding load with the friction measurement system to study the effect of surface roughness on the adsorption gases. We found existence of low friction coefficient about 0.03 on a Cu sample with surface roughness about 90nm under the load of 0.1N at an atmospheric pressure. The load with over about 0.2N and under about 0.05N also showed increasing friction coefficient at an atmospheric pressure. We can understand change of friction coefficient by using Stribeck-Diagram. The diagram shows the existence of regions indicating solid lubrication, boundary lubrication, mixture lubrication and hydrodynamic lubrication by assuming adsorption layer as lubricant on nano surface roughness. It is therefore concluded that the surface with 100nm roughness exhibiting similarly low friction in a vacuum as at an atmospheric pressure is ideal modified surface for residual adsorbed gases layer system to act as fluid lubricant.

VT-TuP5 New Approach to the Calibration of 10 torr Precise Vacuum Gauges*, **S.Y. Woo**, I.M. Choi, B.S. Kim,* Korea Research Institute of Standards and Science, Korea

Capacitance diaphragm gauges (CDG) are electromechanical pressure sensors in which the displacement of a stretched thin metal diaphragm is detected by a capacitance measurement. These are very accurate gauges and frequently used as transfer gauges. In order to calibrate such accurate vacuum gauges, precise mercury manometers have been used. However, complexity, harmfulness of mercury vapor, and cost of mercury manometers made it difficult to use in many calibration laboratories. As a substitute, a gas-operated piston gauges can be used for calibration of such vacuum gauges. But it is difficult to use them for low pressure measurements, because the pressure must be balanced against the weight of the piston, which generally corresponds to a pressure of several kilopascals. To reduce this minimum operating pressure, we adopted a variable bell-jar pressure method. We also developed a new home-made automatic mass loading apparatus which makes it possible to add or remove weights easily without breaking the vacuum during the calibration. Our calibration system can be used to measure pressures from 100 Pa to 2 kPa in the absolute mode. In this paper, practical calibration results are given for two different CDGs in the range of 10 torr full scale.

VT-TuP6 A Real Time Quantitative Diagnostic Technique for Measuring CVD Precursors*, **J. Yun,*** Korea Research Institute of Standards and Science, South Korea, S. Korea*; B. Ahn, J. Kim, Y. Shin, K. Chung,* Korea Research Institute of Standards and Science, South Korea

We present a technique for monitoring the precursor consumption in a chemical vapor deposition (CVD) system. CVD involves chemical reactions that transform gaseous precursors into a solid material in the form of thin film or powder on the surface of a substrate. Precursor costs are a significant factor, and therefore, methods for monitoring precursor consumption are desirable. One diagnostic solution is to use an ultrasonic sensor to determine the precursor liquid level in the CVD containers. This method has advantages in being a noncontact and inexpensive method. It includes an ultrasonic sensor, an ultrasonic generator/receiver, and a computer system that includes an A/D board. The time between the sending of the ultrasonic signal and the return of an echo is used to determine the CVD precursor level in the container. The level of liquid (d) in the container is given by d = V.{(1/2)t}, where v is the velocity of the ultrasonic pulse, and t is the time of flight of the ultrasonic pulse reflected from the surface of the liquid. We got the results obtained from a container with different liquid precursor levels (2, 4, and 6 cm). The accuracy and consistency of the measurements were within an acceptable tolerance range for the three liquid levels (Actual fill level : 2, 4, and 6 cm/Estimated fill level : 2.1, 3.8, and 5.9 cm) In summary, a sensor based on an ultrasonic technique has been developed for monitoring precursor consumption in an CVD system. The prototype sensors developed in this study are expected to be used successfully in semiconductor fabrication.

VT-TuP7 A Comparative Analysis of Four Stanford Research Systems Quadrupole Residual Gas Analyzers Through Quantitative Helium Leak Detection Measurements*, **P.A. Adderley**, M. Poelker, M.L. Stutzman, G.R. Myneni,* Thomas Jefferson National Accelerator Facility

Over the past 10 years, quadrupole residual gas analyzers (RGAs) have become common vacuum diagnostic instruments. Much of the proliferation of this technology throughout the scientific community is due to the high reliability and relatively low cost of the modern RGAs. Jefferson Lab uses over 70 of these devices to diagnose vacuum limitations of the Ultra High Vacuum photoemission guns, monitor hydrocarbon contamination during production of superconducting radio frequency (SRF) accelerator cavities, and monitor helium processing in the SRF cavities. By far, the dominant use of the RGAs at Jefferson Lab is for leak detection. In this paper, we compare the performance of four RGAs from Stanford Research Systems and present detailed procedures that should be used in order to routinely obtain reliable and quantitative measurements of helium partial pressure.

VT-TuP8 Secondary Electron Yield Measurements of TiN Coating and TiZrV Getter Film*, **F. Le Pimpec**, R. Kirby, F. King, M. Pivi,* SLAC

In the beam pipe of the positron Main Damping Ring (MDR) of the Next Linear Collider (NLC), ionization of residual gases and secondary electron emission give rise to an electron cloud which can cause the loss of the circulating beam. One path to avoid the electron cloud is to ensure that the vacuum wall has low secondary emission yield and, therefore, we need to know the secondary emission yield (SEY) for candidate wall coatings. We report on SEY measurements at SLAC on titanium nitride (TiN) and titanium-zirconium-vanadium (TiZrV) thin sputter-deposited films, as well as describe our experimental setup.

VT-TuP9 Photon Stimulated Desorption of the Low Temperature Aluminum Chambers for the Superconducting Wiggler*, **G.Y. Hsiung**, J.Y. Yang, C.C. Chang, S.N. Hsu,* NSRRC, Taiwan*; J.R. Chen,* NSRRC, NTHU, Taiwan

A Superconducting Wiggler, SW6, has been installed in the 1.5 GeV electron storage ring of Taiwan Light Source (TLS) to obtain higher brilliance hard X-ray synchrotron light. The beam duct for the SW6, made of A6061 aluminum alloy, is operated at a temperature of ~ 100 K. It was concerned the gas molecules desorbed from exposure to the scattered light will be reabsorbed and piled up on the surface oxide layers that is difficult to be removed. To evaluate the photon stimulated desorption (PSD) from the low temperature beam duct, a test chamber has been installed in the 19B1(PSD) beam line of TLS for synchrotron light exposure at a critical photon energy of 2.14 keV. The yield of PSD is measured by a throughput method. The chamber was cooled by liquid nitrogen from outside. The residual gas analyzers measure the gas species that reflects the PSD behavior. The result for the beam test at the beam line will be described and the commissioning for the SW6 in the storage ring will also be addressed.

VT-TuP10 Characteristics of the Axial-symmetric Transmission Gauge on the Pressure Measurement in the Vacuum Environment including Ions and Electrons*, **N. Takahashi**, Y. Tuzi,* ULVAC Inc., Japan*; I. Arakawa,* Gakushuin Univ., Japan

The pressure reading of an ordinary ionization gauge is disturbed by the detection of electrons and ions generated outside of the gauge. The elimination efficiency of the axial-symmetric transmission gauge (AT gauge) for the disturbances was examined by the external sources of electrons and ions designed for this purpose. The electron source was composed of a tungsten filament and an electron collector. The ion source was made from a BA gauge from which the top electrode of the grid was removed so that ions escaped out of the ionizer. For comparison, a BA gauge and an extractor gauge were examined under the similar condition of the AT gauge. The pressure readings of BA gauge and extractor gauge showed very low pressure when the external electron source was running. In contrast, the readings of the AT gauge was not affected by the external electron source, because the ion collector is shielded by cover electrode and the retarding field for the electron is created by the end plate of the Bessel-box type energy analyzer in the AT gauge. The gas phase ions generated in the ion source of the AT gauge and ions from the external source was clearly separated in the energy spectra of AT gauge. The spectra were obtained by scanning the path energy of the analyzer of the AT gauge. The pressure measurement without the effect of ions from the outside of the gauge is made by the proper adjustment of the path energy of the analyzer. The energy analyzer in the AT gauge works as a cut off filter for the charged particles coming from the outside of the gauge as well as the original role for the rejection of the soft x-rays and ESD ions generated in the ionizer.

VT-TuP11 Novel Modular Controller for Quadrupole Mass Spectrometers*, **N. Mueller**, S. Foster, G. Peter,* Pfeiffer Vacuum

High performance single quadrupole mass spectrometers nowadays are used in a very wide range of applications. Some examples are accurate residual gas analysis down to the XHV range, vapor beam analysis and control in UHV-MBE tools, isotope ratio measurements, quantitative gas analysis in e.g. catalytic research, and process control in the chemical, pharmaceutical, and metallurgical industry. The very different demands of these applications can be fulfilled by very flexible and modular mass spectrometer controllers only. A novel system contained in a only 3u high 19 inch rack system has been developed that shows the following key features: Intel X-scale processor based controller with Windows CE.net operation system; high speed digital signal processor for mass spectrometer control and data acquisition to allow for scan rates down to 125 microsec / amu; communication to host computer via USB or Ethernet for network operation using OPC standards; fieldbus module to communicate with standardized industrial input / output modules; webserver for control of the system without the need for specific software; modular ion source supply with digital emission current controller for easy adaptation to different filament types, and individually exchangeable voltage supplies for ion lenses; voltages can be biased up to +/-1000V and polarity can be changed to detect positive as well as negative ions; ion counter for count rates up to 130MHz; high voltage supplies for operation various SEMs; autorange control for electrometer amplifiers; analog and digital input / output module for easy connection to external measurement and control devices. In combination with a wide selection of quadrupole rod systems, RF stages, ion sources and ion optics, this system allows for numerous applications from basic research to industry. Detailed functional description as well as data from selected applications will be presented.

VT-TuP12 The Development of a New Vacuum System for the Injection Section of the TLS*, **C.K. Chan**, G.Y. Hsiung, K.Y. Kao, S.N. Hsu, J.Y. Yang, J.R. Chen,* NSRRC, Taiwan

A new vacuum system for the injection section of the Taiwan Light Source (TLS) has been developed for improving the vacuum condition and the injection condition. The major problems to be solved include a higher heat load and a higher pressure rise from a superconducting wavelength shifter (SWLS), in-sufficient linear pumping speed near the ceramic chambers for the kickers and the injection chambers, et al. The new vacuum chambers to be replaced include (a) new kicker chambers, with thinner and wider aperture, with interior uniform Ti-coating for better injection efficiency and for preventing from SWLS irradiations; (b) new aluminum alloys vacuum chambers with interior NEG-coating for higher linear pumping speed; and (c) new beam duct for SWLS with lower outgassing rate. The pressure profile calculated by a computer program shows that the average vacuum pressure can be improved about 5 times lower based on this design. The results of the simulation and the vacuum test for the new chambers will be described.

VT-TuP13 A Compact UHV-compatible Microprober with a Variable-Temperature Sample Stage*, H. Bando*, *Y. Aiura,* National Institute of Advanced Industrial Science and Technology, Japan*; A. Urata,* International Servo Data Corp., Japan*; I. Konishi,* Ibaraki University, Japan*; Y. Nishihara,* Iaraki University, Japan

A compact ultra-high-vacuum-compatible microprober with a variable-temperature sample stage, which is suitable for in situ surface conductivity measurements, is presented. The equipment fits in a space of 300 mm x 300 mm x 100 mm. The vacuum chamber consists of a CF114 nipple with four CF70 and four CF34 ports. Each of four microprobes is position-controlled by a 3D stage made of stainless steel placed outside of the chamber through a CF34-based wobble stick. The bellows of the wobble sticks are of small diameter, allowing use of less-robust 3D stages. A variable-temperature sample stage is fixed symmetrically at the center of the chamber to minimize the thermal drift.

VT-TuP14 The Effect of Dissolved Nitrogen Gas on the Density of Octoil-S --Working Fluid of the NIST 140 Pa Oil Ultrasonic Interferometer Manometer (UIM) Pressure Standard*, J. Hendricks*, *A.P. Miiller,* National Institute of Standards and Technology

The NIST Low Pressure Manometry Laboratory provides primary national pressure standards ranging from 0.01 Pa to 360 kPa. The topic of this presentation is the study of the density of octoil-s, the working fluid the NIST 140 Pa oil UIM which is the current NIST standard covering the pressure range from 100 Pa down to 0.01 Pa. The oil manometer was developed to avoid the ~ 0.2 Pa room temperature mercury vapor pressure that limits the lowest absolute pressure that can be measured with the NIST 360 kPa, and 160 kPa mercury UIMs. The NIST 140 Pa UIM is used to calibrate customer pressure transducers such as Capacitance Diaphragm Gauges (CDGs) of the appropriate Full Scale (FS) range, 0.1 torr, 1 torr, and the bottom ranges (0.01 FS and 0.1 FS) of 10 torr CDGs. The relative change in density of octoil-s as a function of nitrogen gas pressure was determined using a vibrating tube densimeter with a manufacturer's stated uncertainty of 5x10@super -6@ g/cm@super 3@ and a repeatability of 1x10@super-6@ g/cm@super 3@. Results will be presented showing that the effect of dissolved gas on the density of octoil-s does not contribute significantly to the uncertainty of the 140 Pa oil UIM. In addition, the results show that the performance of a planned 1,400 Pa oil UIM will not be adversely impacted by this effect. Finally, planned integration of the densimeter to the NIST oil UIM will allow periodic checks of the density of the manometer fluid should contamination be suspected.}

VT-TuP15 Vacuum Conditions in the Vicinity of a Field Emitter*, M. Zumer,* *B. Zajec, V. Nemanic,* Jozef Stefan Institute, Slovenia

A basic characterization of novel field emitters is usually realized in a standard UHV chamber equipped with appropriate pumps. Their high pumping speed and the remote location of the vacuum gauge prevents to monitor the pressure changes during operation of the field emitter (FE). In most of the potential applications the FE runs in a small sealed device where the local pressure is frequently unknown and its influence on the device lifetime is often underestimated. A small glass envelope equipped with a miniature ion getter pump (IG), spinning rotor gauge (SRG) and a cathodoluminescent screen, was prepared to monitor properly these phenomena. The IG discharge current was calibrated versus pressure by the means of the SRG. Single-crystalline nanoparticles deposited onto molybdenum needles were used as field emitters. The initial pressure in a well outgassed envelope was in the UHV range, but its increase for three orders of magnitude was detected when the field emission current reached one microampere range at 1kV. A good correlation between the FE current and electron stimulated desorbed gases was found.

VT-TuP16 Vacuum Improvements in the ISAC Low Energy Beam Transport Line for Reducing Beam Loss*, D. Yosifov*, *I. Sekachev,* TRIUMF, Canada

Abstract: The TRIUMF 500 MeV cyclotron delivers proton beam currents up to 100 Î¼A into a dedicated beam line and target system for the production of radioactive ion beams (ISAC). Various radioactive species are produced in the target, which are then ionized and extracted. The ions pass through a mass separator and are transported via a low energy beam transport line to experimental areas or injected into an RFQ accelerator. The existing 14m section of the transport line is pumped by two 500 l/sec, and one 1000 l/sec turbo pumps to achieve an average beam on operating pressure of better then 3.0E-7 Torr. The calculated vacuum required to reduce beam losses due to ion collisions with the residual gas to 0.1%/m for high charge state ions is 2.0E-8 Torr. The outgassing rates for some materials used in the beam lines have been measured at TRIUMF and compared with available tabulated data. In the order to improve the vacuum in the beam line section with the highest outgassing rate a cryopump was installed and vacuum change monitored. A bake out test of a beam line section is also scheduled. This paper reports on the results from the vacuum improvement tests and some related calculations.

VT-TuP17 Study of the Pump Pumping Performance after Heat is inputted into the Refrigerating Head of Cryopump*, H.-P. Cheng,* National Taipei University of Technology, Taiwan, Taiwan, R.O.C*; C.-W. Sun, Y.-C. Lu,* National Taipei University of Technology, Taiwan

This study places the heater on the second refrigerating head of Cryopump of closed loop Gifford-McMahon (G-M) that uses helium for refrigerant, and applies different energy on the heater to investigate the pumping performance of Cryopump. The test system is constructed based on the test specification suggested by Welch, the Cryopump model is ULVAC-10PU. Pirani gauge and ion gauge are placed around the chamber to measure the chamber pressure. Before heat is transferred to the heater, the nitrogen and argon pumping speed of the pump is 919~2,170 liter/sec and 1,770~4,060 liter/sec, respectively. After heat is transferred to the heater, when the input watt increases, the temperature of cryopanel surface increases and pumping performance decreases. In the experiment of nitrogen gas, the heater is inputted with 2.5W, 5W, 7.5W, 10W, 12.5W, 15W, 17.5W, of which the decrease in pumping performance is the most apparent in 17.5 W; the pumping speed dropped to 230~625 liter/sec. The corresponding gas throughput is 0.2~63 SCCM. The tested chamber pressure is 1.6E-03~3.0E-01 Pa. In the experiment of argon gas, the heater is inputted with 2.5W, 5W, 7.5W, 10W, 12.5W, 15W, of which the decrease in pumping performance is the most apparent in 15 W; the pumping speed dropped to 507~1,350 liter/sec. The corresponding gas throughput is 0.28~63.45 SCCM. The tested chamber pressure is 1.0E-03~1.5E-01 Pa.

Applied Surface Science
Room 210A - Session AS-WeM
Chemometric Analysis of Spectral or Image Data; XPS/TOF-SIMS Applications

Moderator: J.E. Fulghum, The University of New Mexico

8:20am **AS-WeM1 Angle-resolved X-ray Photoelectron Imaging of Heterogeneous Polymer Samples***, **K. Artyushkova**, J.E. Fulghum,* The University of New Mexico

ARXPS has been widely used for thickness calculations, discerning molecular orientation, and estimating both surface enrichment and concentration gradients. For multicomponent heterogeneous samples not only the average concentration but morphology and chemical heterogeneity are important. In this work we demonstrate the results of combining ARXPS and imaging for analysis of polymer blend samples. Challenges in combining the two approaches include locating the same area for image acquisition at multiple take-off angles, the small depth of focus in imaging mode, and the geometrical transformation of images with changing take-off angle. The conversion of the original photoelectron images to a volume representing the top 3-10 nm of the polymer blend includes principal component analysis, spatial image transformation to correct for geometry or image warping, automatic image registration, mapping images to concentration with the assistance of AR small area spectroscopy, image morphing and visualization. AR images were used to create volumes from the top 3-10 nm of blends of polyvinylchloride (PVC) and polymethylmethacrylate (PMMA) or polystyrene (PS). These volumes allow for the visualization and estimation of the degree of surface segregation and separation of polymer phases. This work has been partially supported by NSF CHE-0113724.

8:40am **AS-WeM2 Detection of Small Chemical Changes on Liquid Crystal-Aligning Polymer Surfaces using Multivariate Data Analysis of XPS Spectra***, **S. Pylypenko**, K. Artyushkova, J.E. Fulghum,* The University of New Mexico

Ion beam alignment of liquid crystals is one of several non-contact methods under investigation as a substitute for mechanical rubbing. The characterization of Ar+ ion beam modified polymers is required in order to understand the macroscopic and microscopic alignment mechanisms. Polymer alignment layers, including polyimide and polystyrene, were studied using X-ray Photoelectron Spectroscopy (XPS) to characterize chemical changes and the surface anisotropy of the alignment substrate. XPS spectra were acquired from samples before and after bombardment, after exposure to the atmosphere, and after 90 degree rotations. XPS spectra of the polymers are dominated by changes resulting from Ar+ ion beam exposure, but also contain smaller changes related to chemical anisotropy. The effect of surface oxidation resulting from the high reactivity of the polymer surfaces after bombardment also must be taken into consideration when interpreting the spectra. We used multivariate analysis to differentiate between chemical changes from ion beam bombardment and oxidation versus the small changes due to chemical anisotropy created by the ion bombardment. Spectra manipulation, including subtraction, and multivariate analysis using Principal Component Analysis (PCA) and Multivariate Curve Resolution (MCR) allowed us to extract information about small changes due to chemical anisotropy. The anisotropy, and associated liquid crystal alignment, result from selective destruction of the weakest bonds relative to the direction of ion beam bombardment.

9:00am **AS-WeM3 Identifying Surface Chemical Changes with XPS Spectral Imaging and Multivariate Statistical Analysis@footnote 1@***, **D.E. Peebles**, J.A. Ohlhausen, K.R. Zavadil, M.R. Keenan, P.G. Kotula,* Sandia National Laboratories

Imaging X-ray Photoelectron Spectroscopy (XPS) allows the distribution of elements and chemical states to be mapped across a surface region of interest. Conventional use of XPS mapping involves utilizing images acquired at peak intensities for chemical species of interest with the subtraction of a suitable background image off the peak. Both peak and background image energies need to be determined from a prior spectrum taken from the imaged region to insure optimal energy selection. While this allows differentiation of chemical states, image contrast and resolution may be poor, especially for overlapping spectral peaks. A more complete and definitive picture of the distribution of chemical species across the surface may be obtained by acquiring a series of images over an energy range that covers the peaks of interest. This generates a very large amount of data that must be processed and correlated, generally with some form of multivariate statistical analysis. Many types of multivariate statistical analyses require user input for the number of species present and their general lineshape. Others produce non-physical spectra that may be difficult to interpret. Multivariate statistical analysis methods developed at Sandia National Laboratories facilitate the rapid analysis of the large quantities of data produced by spectral imaging in an efficient manner without user bias or input. The use of these methods for XPS spectral images to detect changes in chemical state will be demonstrated. In particular, examples illustrating the ability of these techniques to resolve overlapping peaks and reveal correlated species will be included. @FootnoteText@ @footnote 1@ This work was completed at 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.

9:20am **AS-WeM4 Algorithm for Improved XPS-Imaging***, **S. Tougaard**,* University of Southern Denmark, Denmark

Non-destructive XPS-imaging of surfaces is based on analysis of peak intensities. It is however well known that XPS-quantification from the peak intensity leads to huge uncertainties because the measured intensity depends strongly on the depth distribution of atoms. The problem was basically solved by developing models for the detailed analysis of the energy distribution of emitted electrons leading to algorithms summarized in.@footnote 1@ The validity of these algorithms have been extensively tested experimentally and found to be able to accurately determine both the quantitative amount of atoms as well as their in-depth distribution within the outermost ~ 5-10 nm of surfaces. Practical application of these algorithms has increased after ready to use software packages were made available and they are now used in labs worldwide. These software packages are easy to use but they need operator interaction. They are not well suited for automatic data processing and there is a need for simplified strategies that can be automated and used in e.g. XPS-imaging where the huge amount of data hinders manual data analysis. In this paper we study a very simple algorithm that automatically takes the XPS-peak attenuation effect into account@footnote 2@. The algorithm is less accurate than those in@footnote 1@ but it is substantially more accurate than using peak intensities and it is well suited for automation. It gives the amount of atoms within the outermost ~ 3IMFP with a good accuracy and it gives also a rough estimate for the in-depth profile. In the talk, the validity of the simple algorithm is tested on several experimental systems and the results are compared to analysis of the same samples quantified by more accurate methods. The algorithm seems promising for significant improvements in XPS-imaging. @FootnoteText@ @footnote 1@ S. Tougaard, J. Vac. Sci. Technol. A14, 1415 (1996); see also www.quases.com@footnote 2@ S. Tougaard, J. Vac. Sci. Technol. A21, 1081 (2003).

9:40am **AS-WeM5 Chemometric Techniques for Two-way, Three-way and Higher-order Image Data***, **J.M. Shaver**,* Eigenvector Research, Inc., US*; B.M. Wise,* Eigenvector Research, Inc. **INVITED**

Historically, analytical instrumentation would measure a single response such as intensity or counts as a function of a single parameter such as incident energy (e.g. a spectrum). When this response is measured for a range of samples, one obtains "two-way" data. Each sample gives a single vector of responses. A wide variety of numerical analysis techniques exist for performing quantitative and qualitative analyses of two-way data. However, an increasing number of instruments measure response as a function of multiple parameters such as position on the sample, incident energy, and energy of response. Add to these the measurement of multiple samples and the data can become quite complex with respect to relationships between parameters. One method of analyzing such data is to focus on only one parameter at a time (sample vs. incident intensity) or, alternatively, to ignore the relationship between parameters and string the data into one long series of responses per sample. An more sophisticated approach arranges the data into a multi-way array which can be analyzed for relationships between controlled parameters as a function of sample. This often allows improved accuracy and specificity and, in some cases, is even easier to analyze because of the interrelationships. This paper will discuss the concept of multi-way data and some of the issues associated with its analysis, with particular note to multi-way spectroscopic images.

10:20am **AS-WeM7 Maximum Likelihood Principal Component Analysis of ToF-SIMS Spectral Images***, **M.R. Keenan**,* Sandia National Laboratories

Many modern surface analytical instruments are able to acquire huge amounts of data in the form of spectral images. ToF-SIMS, for instance, can easily generate a complete mass spectrum at each point in a 2D or 3D spatial array. The challenge for the data analyst, then, is to garner the analytically useful information from the overwhelming quantity of raw spectral data. Factor analysis techniques such as Principal Component Analysis (PCA) have proven quite useful in this endeavor. Standard PCA, however, assumes that noise in the data is uniform, that is, that it does not depend on the magnitude of signal. This is clearly not correct for methods that rely on particle counting where the noise is governed by Poisson statistics. In this case, properly accounting for heteroscedasticity is essential to extracting the chemical information into a minimum number of factors while maximally excluding noise. Maximum Likelihood PCA (MLPCA) is one approach to addressing this issue. MLPCA can, in principle, incorporate a separate uncertainty estimate for each individual observation in a data set. This paper will present a MLPCA analysis of a simple and intuitive ToF-SIMS spectral image. The results show that there is a tradeoff between the number of uncertainty parameters included in the model and the quality of each and, in fact, using poor estimates may be worse than doing nothing at all. The best results were obtained by using a low-rank approximation to the noise rather than individual estimates. MLPCA will also be compared with an optimal scaling approach. For the particular example given, the added benefits of MLPCA probably do not outweigh the greatly increased computational demands of the technique. This work was completed at 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 **AS-WeM8 AXSIA Analysis of TOF-SIMS Spectral and Image Series Data@footnote 1@***, **J.A. Ohlhausen**, K.R. Zavadil, R.D. Kilgo,* Sandia National Laboratories

AXSIA (Automated eXpert Spectral Image Analysis), a patented multivariate approach invented at Sandia National Laboratories, is used to provide comprehensive analysis of spectral series and spectral image series. We directly compare spectra from many different samples (spectral series) and compare spectral images from different specimens or locations (spectral image series) using this statistical approach. This method of analysis provides full spectral separation of distinct components present within the system of interest. Component variation is expected with fragmentation changes resulting from aging, contamination, concentration, molecular orientation, and chemical reaction. We use spectral series analysis to understand how component variation might be impacted by monolayer deposition and coverage. Spectral series analysis with AXSIA shows promise in extracting a more quantitative determination of the effect of saturation coverage and molecular orientation on fragmentation patterns. We have also been able to process large, complex image datasets containing a number of analysis areas at once. By using a technique of merging multiple datasets into one large dataset, a direct comparison of analysis locations is made. The relative amount of contaminant and substrate species as a function of handling and processing conditions are determined. The effects of processing and handling are readily extracted in this chemical system because all data is processed at once. As a result, the information contained in the component analysis is complete and comprehensive. @FootnoteText@ @footnote 1@This work was completed at 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.

11:00am **AS-WeM9 ToF-SIMS as an Important Tool for Fuel Characterization: A Chemometrics Study***, **G. Jiang**, D. Stone, L. Baxter,* Brigham Young University*; B.J. Tyler,* University of Utah*; M.R. Linford,* Brigham Young University

The combustion of coal and biomass provides a significant amount of the energy needs of the world. As expected, there is a series of standardized tests for characterizing these materials. However, these time-consuming analytical methods do not generally provide the chemical information that is necessary to predict and better understand important problems such as NO formation and soot production. Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) is one of the most powerful surface analytical methods in existence. Here we investigate the possibility of using a single ToF-SIMS analysis to characterize coal and biomass as a replacement for many of the tests that currently need to be performed on each sample. But more importantly we look to ToF-SIMS as a tool that can provide data that is rich in chemical information. To handle the enormous quantities of data that are produced by ToF-SIMS it has become increasingly common to use chemometrics methods such as PCA, PLS, and cluster analysis. Here we report a chemometrics study of ToF-SIMS spectra of a series of coal and biomass samples. As expected, PCA of ToF-SIMS spectra of coal and biomass show these classes of materials to be distinctly different. In particular, scores and loadings plots of coal and biomass ToF-SIMS spectra show that the coal spectra are dominated by inorganic ions, while the biomass spectra are dominated by organic ions. We also note that data preprocessing has a significant impact on the resulting PCA, where more information appears to be available from the data when normalization and standardization are applied. PLS of biomass data shows excellent agreement between the nitrogen content of these fuels and the ToF-SIMS spectra. In summary, these multivariate analyses help build the case for ToF-SIMS as a useful and powerful tool for fuel analysis.

11:20am **AS-WeM10 A Chemometrics Analysis of ToF-SIMS Spectra of Monolayers on Scribed Silicon***, **L. Yang**, Y.-Y. Lua, G. Jiang, M.R. Linford,* Brigham Young University

While chemomechanical modification of silicon with a variety of reagents is now well established, a significant amount of physical characterization remains to be performed on these new monolayers to understand their structures. Time-of-Flight Secondary Ion Mass (ToF-SIMS) was performed on monolayers on scribed silicon derived from 1-alkenes, 1-alkynes, 1-holoalkanes, aldehydes and acid chlorides. In order to best analyze the vast quantity of data that is produced by SIMS a chemometrics analysis was performed. Principle component analysis (PCA) proved to be a powerful tool for data compression and information extraction. Nine different PCA analyses were performed, including analyses of i) negative, ii) positive, and iii) combination of the negative and positive spectra, using i) normalized data, ii) normalized and mean-centered data, and iii) normalized and standardized data. If only normalization is performed the first PC loses most of its information content, as it mostly relates to the distance between the spectra (plotted as single points in a hyperspace) and the origin. If both normalization and standardization are performed it is difficult to extract information from the data because too much noise is given equal importance with the data. The positive and negative ion spectra contain complementary information. PCA of negative ion spectra gave a good separation of the monolayers according to the types of adsorbates used in monolayer preparation. PCA of positive ion spectra primarily separated the monolayers according to the number of carbons in their precursor. PCA of the combined positive and negative ion spectra is similar to that of negative spectra. Loadings plots showed the variables that best account for the variability in the data. PCA also indicates the presence of a few outliers in a large set of data, which further shows the usefulness of this method for demonstrating and confirming surface quality. The results of this study are an excellent confirmation of monolayer formation on scribed silicon from a series of different precursor molecules.

Biomaterial Interfaces
Room 210D - Session BI1-WeM
Cell-Surface Interactions
Moderator: A. Chilkoti, Duke University

8:20am **BI1-WeM1 Study of Confluent Cell Culture Monolayers by XPS and SIMS***, M. Greenfeld, H.E. Canavan, X. Cheng, B.D. Ratner, **D.G. Castner**,* University of Washington

Adhered cells transform the surfaces on which they are cultured by excreting and remodeling the underlying extracellular matrix (ECM) proteins. As the ECM is known to play a vital role in the processes of differentiation, motility, and proliferation, the characteristics and identity of the ECM proteins excreted by different cells, or by the same cells throughout its lifetime, are of a great deal of interest in biology and surface science alike. Until now, traditional high vacuum techniques such as X-ray Photoelectron Spectroscopy (XPS) and Secondary Ion Mass Spectrometry (SIMS) have played only a minor role in the analysis of the ECM, as traditional cell removal techniques are destructive to both the cells and the underlying ECMâ?"in effect damaging the structure of analytical interest. Recently, poly(n-isopropylacrylamide) (pNIPAM) treated tissue culture polystyrene (TCPS) has been developed as a method to non-destructively harvest intact cell monolayers. Using the low-temperature liftoff technique, cell sheets may be non-destructively removed from surfaces and re-deposited atop new surfaces, achieving multilayer structures of different cell types, such are used for tissue engineering. To date, studies of cells harvested via this method have primarily utilized traditional biological techniques to track the morphology of the cells and the location of their ECM proteins. Previously, we have used XPS and SIMS to examine culture surfaces after cell liftoff and identify the ECM proteins retained. In this work, we present the first application of high vacuum techniques to an examination of cell monolayers harvested by low-temperature liftoff. We find that the presence of proteins in the basal surface of the ECM is easily detected via XPS and SIMS. We then compare the identities and relative amounts of ECM proteins at the apical and basal surfaces of the cell sheet to those retained by the underlying surface.

8:40am **BI1-WeM2 Modeling of Bacterial Attachment Using Lewis Acid-Base Models of Colloidal Adhesion***, **L.K. Ista**, K. Artyushkova, T.M. Madrid, J.E. Fulghum, G.P. Lopez,* The University of New Mexico

Understanding the processes involved in primary bacterial adhesion to solid surfaces is an important step in development of surfaces on which biofilm formation can be controlled. The relationship of the interfacial tensions between the attaching organism, the liquid medium and the solid substratum determines whether or not attachment can proceed. Control of bacterial attachment is most easily addressed, therefore, by control of substratum surface energy. The relationship between surface energy and attachment can be described qualitatively using colloidal models of adhesion, although a definitive quantitative model is still elusive. Most attempts at modeling bacterial attachment have been made using data generated from attachment to commercially available substrata or their derivatives, many of which are chemically ill-defined. Investigation of substratum physicochemistry on the attachment of a marine bacterium is described. Model solid substrata were generated using mixed self-assembled monolayers of @omega@-terminated alkanethiolates on gold. These substrata varied systematically in Lewis acid-base, dispersive and polar characteristics, while controlling for other surface factors that may affect bacterial adhesion. The test bacterial strain was the gram negative, marine bacterium Cobetia marina. The surface energetics of this organism were determined by partition into organic solvents that differed in their surface energy . Attachment of this organism to SAM surfaces was then quantified and modeled using standard Lewis acid base models of colloidal attachment and multivariate analysis.

9:00am **BI1-WeM3 Deconstruction the Cell-Biomaterial Interface***, **J.Y. Wong**,* Boston University **INVITED**

Cells respond to three main categories of physicochemical cues: chemical, topographical, and mechanical. While surface chemistry and topography have been studied extensively, substrate mechanics has only recently been appreciated. Recent technologies of creating surfaces with well-defined chemistry and topography combined with sensitive surface characterization techniques have unquestionably deepened our understanding of surface chemical and topographical effects on cell behavior. In contrast, much less is known about substrate mechanics effects on cell behavior. This talk discusses the types of substrata and characterization methods that have been used to investigate substrate mechanics effects on cell behavior. We also speculate on the relationships between changes in substrate elasticity that occur naturally in vivo (e.g. wound healing) and cellular response. We present recent developments in creating substrata with well-defined mechanical properties in our own laboratory and the major challenges and issues of determining whether substrate mechanics effects are a material-independent phenomenon. We also discuss the effects of combining multiple physicochemical cues on cell behavior. The use of model systems in which chemistry, topography, and mechanics can be independently controlled will facilitate the quest for design principles and material selection rules to control cell response.

9:40am **BI1-WeM5 Supramolecular Structure of Adsorbed Collagen Layers and Influence on Endothelial Cells Behavior***, **C.C. Dupont-Gillain**, E. Gurdak, Z. Keresztes, P.G. Rouxhet,* Universitat Catholique de Louvain, Belgium

The aim of this study is to examine the supramolecular organization of adsorbed collagen and to evaluate its influence on endothelial cells, thereby increasing our understanding of cell-material interactions. Collagen was adsorbed on polystyrene (PS) and plasma-oxidized PS (PSox) in different conditions, likely to affect the supramolecular structure of the adsorbed layers. The collagen layers and their mechanism of formation were examined using atomic force microscopy, quartz crystal microbalance, X-ray photoelectron spectroscopy and radiolabeling. On PS, the adsorbed collagen molecules leave protruding segments in solution, allowing fibril formation at the interface; this increases with concentration and with time. Dewetting of the collagen layer leads to the formation of discontinuous layers with a net-like nanopattern. On PSox, collagen mainly forms a felt of lying molecules. The adhesion of human umbilical vein endothelial cells (HUVEC) was studied on collagen layers adsorbed on PS or PSox and presenting a diversity of supramolecular structures. In presence of serum, HUVEC cells could not adhere to PS. After adsorption of a smooth collagen layer, cell adhesion became high, and increased with the adsorbed amount. However, the formation of fibrils at the interface provoked a decrease of cell spreading. The last trend was also observed on PSox. This may be related to the accessibility of recognition sites, which could be hidden once collagen forms fibrils. In contrast, the spreading of HUVEC cells was enhanced on discontinuous collagen layers compared to smooth, continuous ones. In this case, collagen association was triggered by dewetting, which could change the availability of recognition sites. Moreover, the discontinuous pattern could stimulate the organization of cell surface receptors, or allow coadsorption of proteins secreted by the cells. Further work includes antibody assays to assess the availability of recognition sites on adsorbed collagen.

10:00am **BI1-WeM6 Using Thin Films of Fibrillar Type I Collagen to Investigate a Signaling Mechanism that Mediates Growth Arrest in Smooth Muscle Cells***, **J.T. Elliott**,* National Institute of Standards and Technology **INVITED**

Smooth muscle cells (SMC) on fibrillar collagen activate different signaling pathways, have a minimally spread morphology and appear growth arrested compared to SMC cultured on non-fibrillar native collagen. Because studies suggest that SMC interact with both matrices through the same integrin receptors, it appears that it is the supramolecular fibrils that are responsible for the phenotypic response. We used thin films of fibrillar collagen assembled on hexadecanethiol monolayers to investigate which properties of the collagen fibrils control the proliferation signaling. The films are on average 30 nm thick and composed of collagen fibrils that are microns long and as large as several hundred nanometers in diameter. They also have optical properties that are ideal for both phase and fluorescence microscopy. When the fibrillar films are kept hydrated, they induce a growth arrest response in SMC that is similar to the response that is observed on fibrillar collagen gels. If the thin films are dried for several hours before rehydration, the SMC exhibit a well-spread proliferative phenotype and begin to proliferate. Atomic force microscopy (AFM) analysis of these fibrillar films indicates that they are nearly identical in topography, density of fibrils and size of fibrillar structures. These data suggest that the presence of collagen fibrils alone is not sufficient to induce the growth-arrested phenotype. AFM imaging of the fibrillar films under aqueous conditions suggest that the flexibility of the collagen fibrils is reduced during the drying process. We hypothesize that the mechanical properties of the fibrils are an essential determinant of the SMC growth-arrest response. We are currently using live-cell microscopy to understand how these cells interrogate the mechanical properties of collagen fibrils when deciding their phenotypic state.

10:40am **BI1-WeM8 Engineering of Functional Three Dimensional Cell Structures by Inkjet Printing***, **T. Boland**, P. Kesari, T. Xu,* Clemson University*; D. Varghese,* Southampton General Hospital

Tissues and organs exhibit distinct shapes and functions nurtured by vascular connectivity. In order to mimic and examine these intricate structure-function relationships, it is necessary to develop efficient strategies for assembling tissue-like constructs. Many of the top-down fabrication techniques used to build microelectromechanical systems including photolithography are attractive due to the similar feature sizes, but are not suitable for delicate biological systems or aqueous environments. A bottom-up approach using inkjet printers has been proposed to pattern functional cell structures in three dimensions. The freeform cell structures created by the inkjet method are viable and show mature character as exemplified by the contractile responses of smooth muscle cell tubes. These results show promise of the inkjet method for vascular tissue engineering and other applications.

11:00am **BI1-WeM9 Nanofabrication of a Novel Cell Array on Ultrathin Hydrophilic Polymer Gels Utilizing Electron Beam Irradiation and UV Excimer Laser Ablation***, **M. Yamato**,* Tokyo Women's Medical University, Japan **INVITED**

Many methods for surface patterning presented to date are based on lithography techniques and microfabrication onto silicon or glass substrates. Here, we show a novel method to prepare patterned surfaces on polystyrene substrates by grafting ultrathin cell-repellent polymer layers utilizing both electron beam (EB) polymerization and local laser ablation techniques for microfabrication. Polyacrylamide(PAAm) was grafted onto tissue culture polystyrene (TCPS) dishes using electron beam irradiation. Water contact angles for these PAAm-grafted TCPS (PAAm-TCPS) surfaces were less than 10° with grafted amounts of PAAm of 1.6 mg/cm@super 2@ as determined by FT-IR/ATR method. UV excimer laser (ArF: 193 nm) ablation resulted in the successful fabrication of micropatterned surfaces by exposure of the basal polystyrene layers. Many cell types adhered only to the ablated domains after pretreatment of the patterned surfaces with optimized concentration of fibronectin solution. The ablated domain sizes have significant influence on the number of cells occupying each domain. Cell patterning functionality of the patterned surfaces was maintained for more than 2 months without losing pattern fidelity. Utilization of these surface fabrication techniques are also presented for basic cell biology as well as preparation of cell-based biosensors.

11:40am **BI1-WeM11 Evaluation of PDMS as a Model Substrate to Investigate Effects of Substrate Compliance on Cell Behavior: Interplay of Surface Chemistry and Substrate Mechanics*, X.Q. Brown*,** *J.Y. Wong,* Boston University

Polydimethylsiloxane (PDMS) is an attractive model system for studying the effects of tissue mechanical properties on cell behavior, because the elastic modulus of PDMS can be tuned to achieve a physiologically-relevant range. However, it has been suggested that altering crosslink density can also modulate surface properties. Both the chemical and mechanical properties of a substrate can affect cell behavior: while the importance of surface chemistry and substrate mechanics have been studied independent of each other, few studies have considered their integrated effects. In this study, we characterized the mechanical and surface properties of PDMS substrata with different crosslink density and systematically investigated the effect of PDMS crosslink density on vascular smooth muscle cell (VSMC) attachment, spreading and proliferation. We find that after the same surface treatment, the water contact angle of PDMS decreases with decreased crosslink density, whereas the amount of protein adsorbed onto the material surface remains the same. We also find that in the absence of serum, there is a 39% decrease in cell attachment and a 42% decrease in projected cell area as the Youngâ?Ts modulus decreases from 1.79 to 0.05 MPa. Although these differences in VSMC adhesion are diminished in the presence of serum or adsorbed fibronectin, the rate of serum-stimulated cell proliferation is significantly lower on PDMS with higher crosslink density. We conclude that for the range of crosslink density we investigated, the surface properties of PDMS play a major role in controlling the initial attachment and spreading of VSMC, whereas the mechanical properties of PDMS influence the long term growth of VSMC.

Biomaterial Interfaces
Room 213C - Session BI2-WeM
Oligo Nucleotide - Surface Interactions

Moderator: M.J. Tarlov, National Institute of Standards and Technology

9:00am **BI2-WeM3 Characterization of Surface Order and Structure of Thiolated Single-stranded DNA Oligomers on Gold by XPS and NEXAFS*, L.J. Gamble*,** *C.-Y. Lee, N.T. Samuel, H.E. Canavan, D.G. Castner,* University of Washington

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. In this study, we have used x-ray photoelectron spectroscopy (XPS) and near-edge x-ray absorption fine structure spectroscopy (NEXAFS) to characterize the surface order and structure of thiol-terminated ssDNA on gold. While NEXAFS provides an investigation of the order and orientation of the DNA oligomers at a surface, XPS provides a quantitative measure of the amount of DNA at a surface. We find that when thiolated DNA oligonucleotides (T)@sub 16@, (A)@sub 16@, and (A)@sub 8@(C)@sub 8@ are adsorbed to gold surfaces, their surface orientations vary differently with increased adsorption time. Time dependent studies of thiolated (T)@sub 16@ and (A)@sub 16@ oligomers by NEXAFS showed opposite polarization dependence between the two sequences possibly due to differences in their interactions with the gold surface. XPS results also indicate variations in the phosphorus to gold ratios among the three thiolated DNA oligomers over time. Furthermore, we explain these contrasting observations by examining the interaction of unmodified DNA strands that are non-specifically adsorbed to gold. Although polyT does not interact with the gold surface, polyA binds to gold possibly through the amine groups of the bases.

9:20am **BI2-WeM4 Detection of DNA Hybridization by Infrared Absorption Spectroscopy*, K. Miyamoto*,** *Y. Kimura, H. Ishii, M. Niwano,* Tohoku University, Japan

We have previously proposed a new, label-free method of in-situ (in-vitro) determining the chemical bonding conformation of DNA in aqueous solution, by infrared absorption spectroscopy in the multiple internal reflection geometry (MIR-IRAS). In our method, a Si prism, through which infrared lights penetrate, internally reflecting a number of times, serves as an electrochemical electrode. By applying a positive or negative potential to the electrode (prism), we can manipulate negatively-charged DNA molecules in aqueous solutions. In this study, we have selected the chemical system of complementary DNA as an appropriate template for testing the possible application of our method to biosensors for detecting DNA hybridization. We first collect IRAS spectra for complementary single-stranded (ss) DNAs that are comprised of 30 bases, and then analyze the hybridization by observing the spectral changes in the IRAS spectra caused by mixture of the two complementary DNAs in D@sub 2@O solution. We observed significant spectral changes in the frequency region of 1600-1750 cm@super -1@, where the bases of DNA have specific vibration modes (C=O stretching and -NH@sub 2@ scissoring modes) that are quite sensitive to base-paring. On the other hand, no significant spectral changes were observed for mixture of non-complementary DNAs. This confirms that the observed spectral changes were specifically induced by DNA hybridization. Our method would be capable of detecting and classifying other biomolecules such as proteins and peptides.

9:40am **BI2-WeM5 XPS and SIMS Characterization of Oligonucleotide Immobilisation via Patterned Plasma Polymerized Interlayers*, P-C. T. Nguyen*,** University of South Australia, Australia*; R. Metz, S. Kumar,* University of South Australia*; M. DeNichilo,* TGR BioSciences, Australia*; N. Voelcker,* Flinders University of South Australia*; M. Jasieniak,* University of South Australia*; S. Coultas, S. Hutton,* Kratos Analytical Ltd, UK*; H.J. Griesser,* University of South Australia, Australia

Surface immobilised oligonucleotides are an attractive choice as recognition elements in microarrays for parallel, multidimensional, high throughput analysis in many biosensing applications. We investigate the physico-chemical factors affecting efficient oligonucleotide immobilisation and patterning. Furthermore, by using patterned plasma polymer coatings, we implemented a direct, one-step method of fabricating microdot arrays with specific surface chemistries onto which oligonucleotides can be covalently immobilised. Amino terminated oligonucleotides such as 15-T are immobilised via surface aldehyde groups of plasma polymerised polymers. Propanal plasma polymer coatings have been applied to a wide variety of substrates including silicon and Teflon. A mask containing 100 µm diameter holes was used during plasma polymerisation to produce an array of distinct aldehyde surface chemical regions for oligonucleotide immobilisation. XPS analysis of the plasma polymer and the immobilised oligonucleotides gave rise to the expected C, O, N and P peaks. Using atomic concentration, surface coverage is calculated as a measure of immobilisation efficiency. SIMS spectra revealed characteristic thymine containing fragments from the immobilised oligonucleotides. MALDI-MS verified the covalent attachment of the oligonucleotides and their ability to hybridise a complementary strand of 15-A oligonucleotide. Hybridisation kinetics studies are underway. SIMS imaging is used to document the spatial patterns formed by masked plasma deposition and to assess the spatial selectivity of oligonucleotide immobilisation. Small spot XPS will be used to quantify the composition of the microarray dots. Results to date demonstrate that the plasma deposition step, both patterned and unpatterned, is readily transferable to various substrates including Si wafer, Teflon PTFE and Teflon PFA.

10:00am **BI2-WeM6 Molecular Recognition in 2D Binary Mixtures of DNA-Base Molecules Studied by STM*, M. Schöck*,** *R. Otero, L.M. Molina, E. Laegsgaard, I. Stensgaard, B. Hammer, F. Besenbacher,* University of Aarhus, Denmark

Molecular recognition events between complementary nucleic acid bases are fundamental for many biological processes, like DNA replication, and is currently being exploited for self-assembling DNA-based nanostructures. The DNA replication fidelity in living organisms is maintained by a complex molecular machinery of polymerases, exonucleases, etc. On the other hand, in the case of replicating NA molecules in the prebiotic soup, the basic physico-chemical mechanism to steer the replication process is the hydrogen-bonding between DNA bases. The fidelity of this replication process implies that Watson-Crick pairing must be favored over others, like "wobble" or "deviant" pairing. By means of a combination of STM experiments and DFT calculations, in this contribution we compare the 2D molecular networks formed on Au(111) upon deposition of the binary mixtures G-C (purine-pyrimidine pair of complementary bases) and A-C (purine-pyrimidine pair of non-complementary bases). We show that, after a gentle annealing to 80°C the non-complementary bases segregate into islands of pure A and a network of pure C, whereas the complementary bases G and C form a network that cannot be separated by annealing up to the desorption temperature for C. High-resolution STM images allow us to identify the structures for these enhanced thermal stability as structures that contain G-C bonds possibly with the same structure as the Watson-Crick pairs in DNA molecules. This result shows that the hydrogen-bonding interaction alone can steer the molecular recognition process necessary for high-fidelity DNA replication even in the absence of polymerases, exonucleases, etc.,a result that could be relevant to understand the origin and nature of the first self-replicating molecules in the prebiotic soup.

10:20am **BI2-WeM7 Formation of ssDNA Brushes with Controlled Length and Spacing on Gold***, **A. Opdahl**,* National Institute of Standards and Technology*; D.Y. Petrovykh,* University of Maryland*; H. Kimura-Suda,* National Institute of Standards and Technology*; L.J. Whitman,* Naval Research Laboratory*; M.J. Tarlov,* National Institute of Standards and Technology

A method is presented that uses block-oligonucleotides to generate single stranded (ss)DNA brushes with controlled length and density on gold surfaces. The method is based on previously reported observations that adenine oligonucleotides (dA) have a higher affinity than thymine oligonucleotides (dT) for adsorbing on gold substrates (Kimura-Suda, H.; Petrovykh, D. Y.; Tarlov, M. J.; Whitman, L. J.; J. Am. Chem. Soc.; 2003; 125(30); 9014-9015). In this study, adenine/thymine block-oligonucleotides, d(T@sub m@-A@sub n@), with specific (dT) and (dA) sequence lengths, m and n, were adsorbed on gold substrates from aqueous solution and were characterized by FTIR and by XPS. The FTIR and XPS experimental results support a model where the (dA) nucleotides preferentially adsorb on the gold substrate and the (dT) sequences extend away from the substrate. The surface density of the (dA@sub n@) blocks decreases with their length n, such that the overall surface density of (dA) nucleotides adsorbed on the gold is approximately independent of the (dA@sub n@) block length. Therefore d(T@sub m@-A@sub n@) oligonucleotides with long (dA) sequences (larger n) have lower densities of (dT) brush strands in the adsorbed layer. Oligonucleotides with long (dT) sequences, m, are observed to have longer brush strands extending away from the substrate. The n and m dependent adsorption behaviors and the stabilities of the brush layers will be compared to the behavior of alkanethiol derivatized ssDNA monolayers on gold.

10:40am **BI2-WeM8 Coverage and Stability of ssDNA on Gold: Effects of Temperature and Displacement by Alkanethiols***, D.Y. Petrovykh,* University of Maryland and Naval Research Laboratory*; A. Opdahl, H. Kimura-Suda, M.J. Tarlov,* National Institute of Standards and Technology*; **L.J. Whitman**,* Naval Research Laboratory

We characterize self-assembled films of thiolated and unmodified single-stranded DNA (ssDNA) on polycrystalline Au films using Fourier transform infrared (FTIR) and X-ray photoelectron (XPS) spectroscopy. We use homo-oligonucleotides to study the film stability as a function of the DNA-base under conditions used in hybridization experiments. One common method of controlling the ssDNA probe spacing and availability is post-deposition exposure to alkanethiols. Another common post-deposition treatment is exposure to buffer solution at elevated temperature during the hybridization step. In both cases, we find strong base-dependence in agreement with the previous results for film structure and relative adsorption affinities of thiol-modified and unmodified ssDNA [JACS 125, 5219 (2003); 125, 9014 (2003)]. The use of these post-deposition treatments also allows us to compare the relative effects of DNA-DNA vs. DNA-Au interactions for each of the bases. For the three bases that we examined, a wide range of DNA-DNA and DNA-Au interactions is observed: both interactions are weak for oligo(dT); oligo(dA) exhibits a strong affinity for Au surfaces but weak DNA-DNA interactions; and oligo(dC) represents the opposite case, with strong DNA-DNA but weak DNA-surface interactions.

11:00am **BI2-WeM9 Biomolecular Immobilization in a Sugar Polyacrylate Hydrogel***, **M.S. Spector**, P.T. Charles, B.D. Martin, C.M. Soto, C.H. Patterson,* Naval Research Laboratory

A novel sugar polyacrylate hydrogel has been developed as a substrate for high density microarrays. Copolymerization of chemo-enzymatically synthesized 6-acryloyl-@beta@-O-methyl-galactopyranoside with acrylate monomers containing terminal amine or carboxyl functionalities allows for covalent attachment of the oligonucleotides or proteins. The hydrogels show extremely low non-specific adsorption of biomolecules leading to increased signal-to-noise ratio and enhanced immunoassay sensitivity over two-dimensional surfaces. High density microarrays containing oligonucleotides and protein toxins have been obtained using a non-contact microdispensing system onto thin hydrogel films. The large pore size and solution-like environment of these hydrogels allow for easy penetration of large biomolecules and detection reagents. Confocal microscopy was used for three-dimensional visualization of the gel, immobilized biomolecules, and hybridized DNA. Results indicate that DNA diffuses into the hydrogel as discrete spots with higher concentration near the middle of the gel. Hybridization of 70-mer nucleotides was readily observed in these gels.

Magnetic Interfaces and Nanostructures
Room 304A - Session MI-WeM

Magnetic Nanostructures

Moderator: R.A. Lukaszew, University of Toledo

8:20am **MI-WeM1 Structural and Magnetic Properties of Ultrathin Co Film Grown on Pt(100)***, M.H. Pan, K. He, L.J. Zhang, J.F. Jia, Q.-K. Xue,* The Chinese Academy of Sciences, China*; **W.D. Kim**,* Univ. of California at Berkeley and KRISS, Korea*; Z.Q. Qiu,* Univ. of California at Berkeley

Ultrathin Co films were deposited on Pt(100) at room temperature in ultrahigh vacuum, and investigated in situ by Low Energy Electron Diffraction (LEED), Scanning Tunneling Microscopy (STM), and Surface Magneto-Optiic Kerr Effect (SMOKE). The Co film was grown into a wedged shape to provide a continuous change of the film thickness. We find that the Co film forms single crystal ultrathin films at least up to 5ML. For as grown films, we observe only in-plane magnetization. After annealing the film, the Co film develops a perpendicular magnetic anisotropy, leading to a spin reorientation transition at 2.7 ML Co thickness. STM measurements were performed at room temperature both before and after annealing the film. We found very different surface morphology and alloy formation after the film annealing, and attribute the perpendicular magnetic anisotropy to the formation of the Co-Pt alloy layer at the Co/Pt(100) interface.

8:40am **MI-WeM2 Structure and Magnetic Anisotropy of Ultrathin Co Films on Au(111) Vicinal Substrates***, **A. Tejeda**, G. Baudot,* Université Paris 7, France*; A. Coati,* Université Paris XI, France*; Y. Garreau,* Laboratoire Utilisation Rayonnement Electromagnetique, France*; Y. Girard,* Université Paris 7, France*; J.P. Jamet,* Université Paris XI, France*; V. Repain, S. Rohart, S. Rousset,* Université Paris 7, France

Nanostructured systems with magnetization along the surface normal are of technological interest for magnetic storing devices. We have studied ferromagnetic films of Co as they exhibit a strongly enhanced magnetic anisotropy with an easy axis perpendicular to the surface plane. Vicinal surfaces are a system model to control the roughness of the ferromagnetic films. We have deposited Co ultra-thin films on vicinal substrates of Au(111) in order to study the relationship between structure and magnetic properties. STM and Grazing Incidence X-ray Diffraction studies have been performed to determine the surface structure. X-ray diffraction shows that the vicinality of the substrate strongly modifies the Co film structure. While Co/Au(111) presents hcp structure, fcc Co is found on Au(233). Growth on an intermediate surface as Au(788) originates a structure with stacking faults. In a second part, we report on a magneto-optical study of the magnetic properties of these cobalt ultrathin films. In vicinal surfaces, the transition of the magnetisation from out-of-plane to in-plane orientation as a function of Co coverage appears in a more progressive way and at lower coverages than in Co/Au(111). Ex-situ measurements on samples passivated with a gold layer show an helicoidal reorientation transition. The easy axis of the magnetization changes from out-of-plane to in-plane, step parallel orientation. These results will be discussed in the light of the precise structural knowledge of these films.

9:00am **MI-WeM3 Growth and Magnetic Properties of Co Quantum-Platelets on Si(111) Surface***, **Q.-K. Xue**,* The Chinese Academy of Science **INVITED**

Self-organized Co platelets with a singular height and of equilateral triangular shape are fabricated on a Si(111)-7Ã-7 surface pre-decorated with an periodic array of Al magic nanoclusters, as observed using the scanning tunneling microscopy. The selection of such a singular height is attributed to the suppression of chemical reaction between Co and Si by the Al nanoclusters, and the corresponding improved confinement in the motion of the conduction electrons within the Co platelets. Such quantum platelets exhibit intriguing magnetic properties in the hysteresis loop, which is shown to reflect a synergism between magnetic dipole interactions and magneto-crystalline anisotropy of the platelets. The present study demonstrates a promising pathway to directly integrate magnetic nanostructures with Si-based electronic devices. @FootnoteText@ In collaboration with Ming-Hu Pan, Hong Liu, Jun-Zhong Wang, Jin-Feng Jia, Xiang-Rong Wang, J. T. Markert, C. K. Shih, Zi-Qiang Qiu, and Zhenyu Zhang.

9:40am **MI-WeM5 Ferromagnetic Stability in Fe Nanodot Assemblies on Cu(111) Induced by Indirect Coupling through the Substrate*, M.A. Torija*[1]**, Oak Ridge National Laboratory, University of Tennessee, Knoxville*; J.P. Pierce,* Oak Ridge National Laboratory, Sandia National Laboratories*; Z. Gai,* Oak Ridge National Laboratory, Peking University, China*; E.W. Plummer,* Oak Ridge National Laboratory, University of Tennessee, Knoxville*; J. Shen,* Oak Ridge National Laboratory

To first order, assemblies of nano-scale magnetic dots are superparamagnetic. In these systems, thermal energy, which causes fluctuation of the dots' magnetic moments, becomes significant enough to overcome the anisotropy energy barrier and randomize their orientation at the so-called blocking temperature. This typically occurs far bellow room temperature. In real nanodots assemblies, it has been generally recognized that the magnetic dipole-dipole interaction can affect the barrier height for flipping the spin of each individual dot as well as the collective magnetic behavior of the dot assembly. In this work, we report collective ferromagnetic behavior in two- dimensional Fe dot assemblies on the Cu(111) surface that persists above room temperature. Our ability to tune the average size and spacing of the dots enables us to investigate the relative contributions of the mechanisms that support this unexpectedly robust magnetic order. Our experimental results and simulations indicate that the high-Tc ferromagnetism cannot be explained by either magnetic anisotropy or dipolar interaction. Direct comparison of the Curie temperatures (Tc) of similar dots prepared on vaious substrates including Cu(100) and Ge(111) allows us to conclude that the observed high-Tc ferromagnetism for Fe dots on Cu(111) is a result of an indirect exchange interaction via the surface states of Cu(111) substrate.

10:00am **MI-WeM6 Exploring New Magnetic Properties in Coupled Magnetic Nanostructures*, C. Won*,** *Y.Z. Wu,* University of California at Berkeley*; A. Scholl, A. Doran,* Lawrence Berkeley National Laboratory*; N. Kurahashi,* University of California at Berkeley*; H. Zhao,* 3 International Center for Quantum Structures, China*; Z.Q. Qiu,* University of California at Berkeley

Interaction between different magnetic entities in a magnetic nanostructure creates new properties that are not available in single phase bulk materials. In order to study how the magnetic interaction at nanometer scale generates new magnetic behaviors, we applied photoemission electron microscopy (PEEM) to investigate coupled magnetic nanostructures. The unique element-specific capability of PEEM allows the measurement of different magnetic species separately, thus enabling the identification of new magnetic properties caused the magnetic coupling. Several systems have been investigated by our group in the last a few years. In this talk, I will first give an overview of the research topics that we studied using PEEM. Then I will focus on a particular topic of magnetic phase transition in coupled magnetic layers. Co/Cu/Ni/Cu(100) and Co/Fe/Ni/Cu(100) are fabricated using epitaxial growth in which the Cu and Fe spacer layers controls the interlayer coupling between Co and Ni films. Element-specific measurements are performed to monitor the ferromagnetic to paramagnetic phase transitions of the Co and Ni films separately. Our results show that the interlayer coupling couples the magnetic fluctuations of the Co and Ni films to result in three types of magnetic phase transitions. A complete phase diagram is constructed in the Co-Ni thickness plane and a Monte Carlo simulation explains the conditions of having these three types of transitions.

10:20am **MI-WeM7 Self-assembled Ferroelectric/Ferrimagnetic BaTiO@sub3@-CoFe@sub2@O@sub4@ Nanostructures*, H. Zheng*[2]**, *J. Wang, Z. Ma, L. Mohaddes-Ardabili, T. Zhao, S.R. Shinde, S.B. Ogale, M. Wuttig, A. Roytburd, L. Salamanca-Riba,* University of Maryland, College Park*; S.E. Lofland,* Rowan University*; D. Viehland,* Virginia Tech*; D.G. Schlom,* Pennsylvania State University*; R. Ramesh,* University of California Berkeley

Ferroelectric/ferrimagnetic BaTiO@sub3@-CoFe@sub2@O@sub4@ (BTO-CFO) nanostructures have been synthesized by pulsed laser deposition using a single Ba-Ti-Co-Fe-Oxide ceramic target. Spinel CFO and perovskite BTO phases spontaneously separated during heteroepitaxial growth on single crystal SrTiO@sub3@ (001) substrates. It is shown that films are epitaxial in-plane as well as out-of -plane, with CFO nano-pillar arrays embedded in a BTO matrix. CFO pillars have uniform size and spacing. As the substrate temperature increases from 750 °C to 950 °C, the average lateral size of the pillars increases from ~9 nm to ~70 nm. Magnetic measurements exhibit that all the films have a large uniaxial magnetic anisotropy with an easy axis normal to the film plane. It is calculated that stress anisotropy is the main contribution to the anisotropy field. We measured the ferroelectric and piezoelectric properties of the films, which correspond to the present of BTO phase. The temperature dependent magnetic measurements illustrate a coupling between the two order parameters of polarization and magnetization by a change in magnetization at the ferroelectric Curie temperature. This approach to the formation of self-assembled ferroelectric/ferromagnetic nanostructures is generic and manifests itself in other such spinel-perovskite systems, thus making it of great interest and value to a broad materials community. This work is supported by the NSF-MRSEC under contract No. DMR-00-80008.

10:40am **MI-WeM8 Artifically and Self Organized FePd(001) Nanoparticles: Fabrication, Magnetic and Magneto-Photonic Properties*, A. Cebollada*,** IMM (CNM-CSIC), Spain*; C. Clavero, A. Bengoechea,* IMM (CNM-CSIC) Spain*; J.L. Costa Kramer, A. Garcia-Martin, J.V. Anguita, G. Armelles,* IMM (CNM-CSIC), Spain*; Y. Huttel,* ICMM (CSIC), Spain*; L.l. Balcells,* ICMAB (CSIC), Spain*; V.F. Puntes,* Univ. de Barcelona, Spain **INVITED**

The fabrication and investigation of ordered arrays of high anisotropy and magneto-optic activity L10 FePd nanoparticles is reported. These arrays of particles are grown in 2 and 3 dimensions and embedded on single crystalline MgO(001) substrates and matrices. The deposition conditions are optimised to obtain the chemically ordered L10 phase. Several approaches are followed to obtain two dimensional nanostructured arrays: self organization, artificial generation of nucleation centres prior to growth and post growth patterning using e-beam lithography and nano-masks. The deposition of an epitaxial MgO matrix that conformally covers the FePd islands allows the subsequent growth of further FePd nano-particle layers, obtaining a 3D array of single crystalline high anisotropy particles embedded in an insulating matrix. The magnetization reversal, inter-particle magnetic interactions and magnetic anisotropies are studied in both 2D and 3D arrays, with special emphasis on the role that the reduction in dimensionality and the chemical and spatial order play in the magnetic properties. The characterization of the magneto optic and magneto photonic properties of these new materials is also performed in the same context.

11:20am **MI-WeM10 Properties of Magnetic Wires, Dots, and Dot Chains Fabricated via Epitaxial Growth*, D. Li,*** Argonne National Laboratory **INVITED**

Manufacturing Science and Technology
Room 303B - Session MS-WeM

Semiconductor Manufacturing Technologies for the 45nm Crisis

Moderator: L. Larson, Sematech

8:20am **MS-WeM1 Integration Challenges for 45nm Strained Si Devices*, M. Sadaka*,** *A. Thean, A. Barr, T. White, B. Nguyen, V. Vartanian, M. Zavala, D. Eades, S. Zollner, Q. Xie, X. Wang, R. Liu, M. Kottke,* Freescale Semiconductor **INVITED**

As power supply voltage becomes lower with successive scaling, the non-scalability of threshold-voltage and conventional gate oxide to maintain

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[1] **Falicov Student Award Finalist**

[2] **Falicov Student Award Finalist**

low stand-by leakage is rapidly reducing the maximum gate overdrive factor. Enhancing carrier mobility by biaxially-straining Si on relaxed SiGe on SOI and on Bulk substrates provides a viable option to sustain the continual drive current increase. Though strained-Si addition to conventional MOSFET seems minimally disruptive, the use of SiGe in CMOS devices introduces new process and device challenges, wafer quality requirements, substrate cost issues, and new metrology requirements for strain monitoring. All these challenges need to be addressed in order to prove successful manufacturability. This talk will focus on the integration challenges of strained Si devices. The process and device challenges include Ge up-diffusion into strained Si channel, dopant diffusion differences between Si and SiGe, NiSi versus CoSi, and the need for raised source drains (formed by selective epitaxy) due to Ge segregation with cobalt silicidation. Wafer quality requirements include reducing the defect density less than 10@super 3@ defects/cm@super 2@ in order to realize yielding, high density large circuits, while maintaining maximum levels of achievable strain at a reduced wafer cost relative to the cost of SOI wafers. Finally, the appropriate metrology specific to strained Si monitoring will be discussed.

9:00am **MS-WeM3 45nm Node Architecture: The Driving Force of the Ion Implantation and Activation Processes Challenges**, ***D. Lenoble***, STMicroelectronics **INVITED**

In the current development of the 65nm node, various technical approaches regarding doping processes have been evaluated to fulfill the technology requirements of poly-gate doping, ultra-shallow junctions, channel and isolation architectures and deep gradual junctions. Low thermal budget processes (solid-phase epitaxy), advanced ion implantation processes (Plasma Doping), advanced activation processes (flash or laser annealing), stressed SiGe junctions, Poly-SiGe gate, offset spacers, 0° tilt wells implants, antimony implants, etc. are some examples of processes that are evaluated by ICMs for the 65nm node. In this paper, we propose to make a review and to discuss each technique to highlight their specific benefits and drawbacks for the manufacturing of a planar 65nm technology platform. Based on this status and on the basic requirements of the 45nm node, we build different scenarios about the major technological or architectural breaks that will emerge. Then, such projections are discussed in term of future technical challenges for the ion implantation and activation processes.

9:40am **MS-WeM5 Taking SOI and Low-k Dielectrics Into 130nm and 90nm High-Volume Microprocessor Production: Challenges, Processes, Extendibility**, ***R. Stephan***, *D. Greenlaw, G. Burbach, T. Feudel, F. Feustel, K. Frohberg, F. Graetsch, G. Grasshoff, C. Hartig, T. Heller, K. Hempel, M. Horstmann, P. Huebler, R. Kirsch, S. Kruegel, E. Langer, K. Romero, H. Ruelke, H. Schuehrer, A. Wei, T. Werner, K. Wieczorek,* Advanced Micro Devices, AMD Saxony LLC, Germany **INVITED**

SOI and Low-k technologies are mature at AMD and run in high-volume production. These technologies were developed for the fabrication of the 9-metal AMD OpteronTM and AthlonTM64 microprocessors.@footnote 1@ The 130nm version has been in production for 18 months, and the 90nm product shipments began several months ago. The paper highlights several challenges found when moving from development to high-volume production. SOI process modules have been developed to support a smooth conversion from 130nm to 90nm. Basic learning can be applied for the extension to the 65nm node. Examples of advanced SOI process modules such as STI, ultra-thin gate dielectrics, gate pattering, and the Cu interconnect using CVD-deposited low-k dielectric will be shown. The early implementation of SOI and low-k dielectrics into high-volume manufacturing will allow for the successful extension into the next process generations. @footnote 1@AMD, the AMD Arrow logo, AMD Athlon, AMD Opteron and combinations thereof are trademarks of Advanced Micro Devices, Inc.

10:20am **MS-WeM7 Beyond Planar Bulk CMOS: Manufacturing Issues in the 3rd Dimension**, ***C.R. Cleavelin***, Texas Instruments **INVITED**

The continuation of highly scaled Planar Bulk CMOS has been identified @footnote1@ as very difficult, if not impossible, at or beyond the 45nm Node due to short channel effects (SCE) and other parasitic effects. Several device structure options for "non-classical" CMOS have been proposed and fabricated in research environments, e.g., Ultra-Thin Body SOI (UTB-SOI) or Multiple-Gate FET (MuGFET) both using lightly doped bodies for scaling gate length Lg well below 20nm. Although these devices offer good device characteristics and scaling opportunities, fabrication and optimization of these devices for device level CMOS integration and production present inherently difficult challenges. This talk will identify and discuss many of these integration roadblocks and manufacturing challenges and discuss possible paths to overcome them. @FootnoteText@ @footnote 1@ International Technology Roadmap for Semiconductors 2003 Edition.

11:00am **MS-WeM9 The Nanotechnology Research Institute**, ***G. Bourianoff***, Intel Corp. **INVITED**

The Semiconductor Industry Association (SIA) has recently called for the creation of the Nanotechnology Research Institute (NRI) which will be dedicated to creating new ideas and demonstrating feasibility for novel electronic switching devices with associated memory and interconnects by the year 2020. The proposed institute will be a joint effort by industry, academia and government involving university faculty and students working with industrial assignees working in state of the art facilities located on or adjacent to university campuses. Funding would come from a partnership between government and industry. This paper will give the latest information on the research program and organizational structure of the NRI. In general, the NRI will address the scientific and engineering aspects of classical information processing at nanometer scale lengths, fempto second time scales and atto Joule energies. It will consider devices and architectures that rely on state variables other than electronic charge such as spin, phase, photons, dipole orientation, magnetic flux quanta, orbital symmetries and other non-stander state variables. It will consider novel architectures that rely on nearest neighbor data flows and novel data representations that may rely on associative data structures. It will seek to understand the relationship between information and entropy and many other advanced concepts that are vital to future scaling.

Nanometer-scale Science and Technology
Room 213D - Session NS-WeM

Nanoscale Patterning and Lithography

Moderator: D.W. Carr, Sandia National Laboratories

8:20am **NS-WeM1 Massive Self-Assembly for Integrated Carbon Nanotube Circuits**, ***S. Hong***, Seoul National University, Korea, South Korea **INVITED**

Nanoscale electronic devices made of carbon nanotubes (e.g. transistors, sensors) can be much smaller and more versatile than any conventional microelectronic chips, while the lack of a mass-production method has been holding back their practical applications. Inspired by biomolecular self-assembly, we developed a novel self-assembly method for the wafer-scale fabrication of millions of carbon nanotube circuits with a single-nanotube-level precision. This method may enable industrial-level production of nanotube-based devices such as faster electronic circuits and high-density sensor arrays.

9:00am **NS-WeM3 Surface-Programmed Assembly of Carbon Nanotubes on Silicon Oxide Surfaces for Integrated Circuit Applications**, ***M. Lee***, *J. Im, S. Hong,* Seoul National University, South Korea

As the microelectronics approaches its resolution limit, alternative electronic devices draw the attention of the scientific community. One strong candidate can be carbon nanotube (CNT)-based electronics. We developed a method to selectively assemble carbon nanotubes at a desired location with precise orientations on silicon oxide substrates. In this process, surface molecular patterns guide the assembly of CNTs onto desired locations. Importantly, we utilized only conventional microfabrication process such as photolithography for the entire process, which makes our method completely compatible with microfabrication techniques. This research can be utilized for fabrication of carbon nanotube-based electric circuits.

9:20am **NS-WeM4 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, Knoxville*; R.J. Kasica, D.K. Hensley,* Oak Ridge National Laboratory*; A.V. Melechko,* Univeristy of Tennessee, Knoxville*; D.C. Joy, P.D. Rack, B. Blalock, S. Islam,* University of Tennessee, Knoxville*; M.A. Guillorn,* Cornell Nanofabrication Facility*; M.L. Simpson,* Oak Ridge National Laboratory

The Digital E-beam Array Lithography (DEAL) concept is currently under development at Oak Ridge National Laboratory (ORNL).@footnote 1@ 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 SiO@sub 2@. The first electrode functions as the cathode and contains a single vertically aligned carbon nanofiber as the field emitter. The second is a 2-

µm diameter extraction aperture formed using a self-aligning process. The third is a 4-µm diameter aperture functioning as an electrostatic focusing lens and created using standard photolithographic processing. 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 good agreement with device modeling. Our current 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. @FootnoteText@ @footnote 1@ ORNL is managed by UT-Battelle, LLC, for the U.S. Department of Energy under contract No. DE-AC05-00OR22725.

9:40am **NS-WeM5 Monomer Based Thermally Curable Imprinting Lithography***, **H. Lee,*** Korea University, Korea

Nanoimprint lithography is one of the most viable technologies for mass production of devices with nano-patterns such as optical components (polarizer and diffuser), bio and NEMS devices, photonic crystals and patterned magnetic media. With this technology, nano patterns are generated by duplicating the ruggedness of imprinting stamp onto polymer films on the substrate. However, high pressure (>800psi) and high temperature (>150C)operation is required to transfer nano patterns onto polymer film. In this study, a mixture of base monomer, vaporization inhibitor, anti-sticking agent and thermal initiator was used as an imprint resin. Viscosity of mixture was controlled by relative amount of vaporization inhibitor. Compared to the polymer based resin such as PMMA, monomer based resin has several advantages. Since the monomer based imprinting resin is in liquid phase without heating up to the decomposition temperature of thermal initiator, high quality pattern transfer with minimized residual layer can be done at much lower imprinting pressure. The decomposition temperature of thermal initiator is relatively lower than the glass temperature of polymer. Thus, imprinting can be done at lower temperature (below 100C). Thus, time consumption for heating and cooling can be reduced and higher throughput was obtained. In this study, whole 6 inch diameter wafers were patterned by single step imprinting with the same sized stamp.

10:00am **NS-WeM6 Charge Interactions in Ferroelectric Substrates: the Basis of Ferroelectric Nanolithography***, **D.B. Li,** R. Shao, D.A. Bonnell,* The University of Pennsylvania

A new approach to directed assembly has recently been proposed that allows multiple nanostructures of diverse materials to be positioned in predefined locations. Ferroelectric Nanolithography has been demonstrated in the assembly of metal nanoparticle/functional organic molecule/oxide systems for a wide range of materials. The process is based on patterning ferroelectric domain orientation to control surface local electronic structure, which can be accomplished with exposure to electron beams and optical interference patterns. The underlying physics of these processes is not understood. This paper examines the effects of electron injection and electron-hole pair generation on surface ferroelectric polarization and charge compensation. The effects of dose, substrate thickness, and substrate morphology on pattern spatial resolution and stability are quantified for lead zirconate titanate and barium titanate films. For the case of electron-hole pair generation the mobile carriers compensate local atomic polarization at the surface. On high dose electron injection an electric field is established which reorients the polarization vectors. Both processes alter the local electronic structure by influencing surface band bending.

10:20am **NS-WeM7 Nanoscale Patterning in Application to Novel Materials and Device Structures***, **N. Zhitenev,*** Bell Labs, Lucent Technologies **INVITED**

As the size of electronic devices shrinks down to atomic scale, device properties are increasingly dependent on physics and chemistry of interfaces or interfacial networks. The growth, the patterning and the characterization of such systems at nanometer scale present significant challenges and opportunities. Extremely small devices can display useful functionality based on new physical phenomena. On the other hand, direct lithography requiring deposition of resists, exposure to radiation and to wet/dry chemistry can strongly modify the device properties. Possible solutions are to perform the most invasive patterning before the growth or out of a potentially delicate device structure. We study such fabrication schemes in application to the patterning of self-assembled molecular monolayers between metal electrodes. The first approach uses pre-fabricated masks to confine the deposition of materials. The size of the features is controlled by shadow angle evaporation. Another method uses nanoimprinting to deliver patterned metal onto molecular layer. Metal-molecular layer-metal junctions are fabricated with the size down to ~10-100 nm. While certain electrical properties are fairly reproducible, these techniques provide only initial foothold toward the fabrication of nanoscale interfacial devices. The critical issues that determine the overall performance and require further research are control of the surface topography and the grain structure of metals, doping of the molecular layers by the contacts and formation of the chemical bonds at the interfaces.

11:00am **NS-WeM9 Fabrication of Nanopatterned Polymer Brushes by Scanning-Probe and Electron-Beam Lithography***, **W.K. Lee,** M. Kaholek, S.J. Ahn, S. Zauscher,* Duke University

Here we present several lithographic approaches that we have adopted to fabricate nanopatterned polymer brushes. We demonstrate the use of nanoshaving, where an atomic force microscope (AFM) cantilever tip is employed as a nanomechanical tool to selectively remove a thiol resist. The freshly exposed gold surface in the resulting â?onano-trenchesâ?⍰ was immediately backfilled with a bromo-thiol initiator and enabled patterned surface initiated polymerization. In a complementary approach we prepared oxide nanopatterns on resist-coated silicon surfaces by applying an electric potential between the AFM cantilever tip and the silicon substrate. In this case the nanopatterns were backfilled with a silane initiator SAM. We show that the choice of silane SAM enables both, ring-opening metathesis and atom transfer radical polymerization. We also used lift-off (dissolution) e-beam lithography (EBL) to generate gold nanopatterns that could again be used to immobilize a thiol initiator. We demonstrate that by choosing an appropriate nanolithography technique and combining it with a suitable polymerization technique allows us to fabricate high-density polymer brush arrays with control over chemical functionality, feature dimension, shape, and interfeature spacing on the nanometer length scale. Furthermore we demonstrate that the spatially controlled immobilization of stimuli-responsive macromolecules on solid surfaces at the nanometer-length scale enables fabrication of â?osmartâ?⍰ â?"externally switchableâ?" polymer nanoarrays. Such nanostructures can provide sensing functionality within integrated nanoscale bioanalytical devices in which the transport, separation, and detection of biomolecules must be performed in aqueous solutions.

11:20am **NS-WeM10 Thermal Control in Dip Pen Nanolithography***, **P.E. Sheehan,*** Naval Research Laboratory*; W.P. King,* Georgia Tech*; L.J. Whitman,* Naval Research Laboratory

Although it has been widely assumed that Dip Pen Nanolithography (DPN) requires a water meniscus to tranfer ink from an AFM tip to a surface, we have shown that transfer can occur under xeric conditions@footnote 1@ , a method we call "dry deposition". Our recent studies of dry deposition have led to a number of insights into how DPN can be extended beyond "wet" inks. For example, deposition should be possible at high temperatures (i.e., above the boiling point of water) and, thus, temperature could be used to control deposition. We have utilized a heated atomic force microscope (AFM) cantilever tip to control the deposition of a solid organic ink. The ink, octadecylphosphonic acid (OPA), melts at 98°C and self-assembles on mica, the substrate. Evaporation was used to coat OPA onto a cantilever with integrated microheaters. When the cantilever temperature was below 98°C, no deposition was detected. At 98°C slow deposition was seen, but only after raising the temperature to 122° C was deposition robust. Thermal DPN (tDN) enhances traditional DPN in many ways. First, it allows exquisite control over writing--deposition may be turned on or off and the deposition rate changed without breaking contact with the surface. Secondly, the inks used have lower surface mobilities once cooled and so are able to achieve higher spatial resolution. Thirdly, imaging with a cool tip does not appear to contaminate the surface. This allows in situ confirmation of the deposited pattern without fear of contamination. Finally, tDPN expands the range of useable inks--current work with electronically active molecules that have high melting temperatures will be presented. @FootnoteText@ @footnote 1@ PRL 88, 156104 (2002).

11:40am **NS-WeM11 Chemomechanically Scribing Silicon with an AFM in a Read/Write Fashion***, M.V. Lee, K. Gertsch,* ***R.C. Davis****, M.R. Linford,* Brigham Young University

One of the most important problems in nanotechnology is the precise positioning of molecules on surfaces. One possible method for accomplishing such nanoscale patterning is the chemomechanical modification of silicon with an AFM tip. Using this method ca. 30 nm functionalized lines have been produced by i) wetting hydrogen-terminated silicon with a reactive compound, and ii) scribing with an AFM tip. Scribing activates the silicon so that it reacts with the liquid it is in contact with wherever the AFM tip is pushed against the surface. The width of the functionalized feature can be controlled by changing the force applied to the tip. In this talk we also report advances in chemomechanically depositing a monolayer on silicon using an AFM, and then chemomechanically replacing the monolayer in the scribed region by scribing over the functionalized region. Time-of-flight secondary ion mass spectrometry is used to confirm surface modifications and alterations. This new read-write capability should significantly increase the usefulness and power of the chemomechanical method at nanometer dimensions. @FootnoteText@ Wacaser, B.A.; Maughan, M.J.; Mowat, I.A.; Niederhauser, T.L.; Linford, M.R.; Davis, R.C. Chemomechanical surface patterning and functionalization of silicon surfaces using an atomic force microscope. Applied Physics Letters 2003, 82(5), 808-810.

Organic Films and Devices
Room 304C - Session OF+EM-WeM

Molecular and Organic Films and Devices - Electronics

Moderator: A. Kahn, Princeton University

8:20am **OF+EM-WeM1 Self-assembled Monolayers in Organic Electronic Devices*****, G. Horowitz****, P. Lang,* ITODYS, University Denis Diderot, France*; W. Kalb,* RWTH Aachen, Germany*; M. Mottaghi, A. Roumiantseva, A. Yassar,* ITODYS, University Denis Diderot, France **INVITED**

The use of molecular materials as active component in electronic devices has recently experience considerable interest. Organic electronic devices are fabricated by piling up several layers on top of each other. Because of that structure, the role of interfaces is crucial in the performance of the devices. An elegant way of controlling the quality of interfaces is the use of self-assembled monolayers (SAMs), which consists of a single layer of molecules chemisorbed on a surface. The molecules are most often based on long alkyl chains that tend to self-assemble to form highly ordered single layers. One end of the chains is substituted with a group capable of inducing chemisorption on the surface, while the other end can be used to control the quality of the modified surface. This technique will be exemplified by two approaches. The first one is a transistor made of a thin film of pentacene deposited on an alumina layer that serves as the gate dielectric. We show that the performance of the transistor is strongly influenced by the modification of the alumina surface by a SAM of a fatty acid. Correlation is made between the structure of the pentacene film and the properties of the transistor. In the second example, the SAM is made of hybrid molecules comprising an alkyl chain connected to a conjugated part (e.g., thiophene or acene). In that case, the SAM constitues the very heart of the device, which may open the way to electronics at the molecular level.

9:00am **OF+EM-WeM3 AFM Study of @beta@-7T Oligothiophene Films on Mica: Humidity-Dependent Mechanical Properties and Structure*****, J.Y. Chen****, I. Ratera, D.F. Ogletree, M. Salmeron,* Lawrence Berkeley National Laboratory*; AR Murphy, JMJ Frèchet,* University of California, Berkeley

Langmuir-Blodgett films of @beta@-7T@footnote1@ oligothiophene, a molecule with potential molecular electronic applications, were transferred to mica and studied with contact AFM. Mono and multilayer films exhibited structural and mechanical properties that depend on humidity, temperature and applied force as well as the LB transfer pressure. We found that monolayers were adsorbed through the carboxylic acid group, exposing the alkyl chains to the air interface. Two structural phases of the molecular film were observed. In the "A" phase the molecules were fully stretched and the film had a height of 2 nm. This phase was stable at high humidity and under low loads. The "B" phase had a height of 1.2 nm and was stable under dry conditions and high loads. Domains of both A and B phases were observed in the same larger islands. Changing humidity reversibly modified the A:B ratio and the sizes of the domains. Heating the samples resulted in an irreversible decomposition of the continuous film islands into small aggregates. @FootnoteText@ @footnote1@ @beta@-7T: a 7 thiophene oligomer with two alkyl side chains and an acetic acid group, 3'',4''''-didecyl-5,2';5',2'';5'',2''';5''',2''''; 5'''',2''''';5''''',2''''''-heptathiophene-4'''-acetic acid.

9:20am **OF+EM-WeM4 Fabrication of High Performance O-TFT Devices with Long Term Stability by using Atmospheric Plasma Treament and Passivation Layer***,* ***W.J. Kim****, H.K. Baik,* Yonsei University, Korea

We report the effect of a surface treament of the various dielectric layers by using atmospheric plasma on the device performance. We also employ the SiO based passivation layer to the top of fabricated devices with plastic-based substrates for the long term stability. With cost-effective atmospheric glide arc plasma treatment, the surface of dielectric layers was modified to fit more well to the organic active layer resulting in the high value of saturation current and field effect mobility. The O-TFT device with our SiO based passivation layer shows good device performance even after it has been exposed to Air in long period of time. Both high performace and long term stablity of the O-TFT devices could be achieved by our cost-effective method.

9:40am **OF+EM-WeM5 Pentacene Thin Film Transistors***,* ***G.G. Malliaras,*** Cornell University **INVITED**

The growth of pentacene films on oxide surfaces plays a major role in determining the device performance. A combination of synchrotron x-ray diffraction and atomic force microscopy was used to probe this interface. In-plane diffraction from films down to one monolayer thick was observed, which allowed to probe the early stages of film growth. Depositions at various substrate temperatures and deposition rates were found to yield films with crystallite sizes from hundreds of nanometers to tens of microns. The performance of these films in thin film transistors was investigated. The scaling of the transistor characteristics down to nanometer size channel lengths is discussed. Finally, applications in sensors are demonstrated.

10:20am **OF+EM-WeM7 OMBD of Organic Semiconductors on Metal Surfaces: Structural and Electronic Properties***,* ***G. Witte****, C. Wöll,* Ruhr-Universität Bochum, Germany

The promising potential of using organic semiconductor materials as active layers for organic electronic applications and the increasing interest in molecular electronics have expressed an urgent necessity of understanding the molecular microstructure and growth properties of ordered organic films. Of particular interest for the fabrication of thin films organic field effect transistors are polycyclic aromatic hydrocarbons which reveal a large variety of structures upon growth on inorganic substrates.@footnote 1@ Here we report results of a comprehensive growth study of pentacene and perylene films on various metal surfaces. By combining LEED, HAS, XPS, NEXAFS, TDS and AFM we were able to characterize the molecular microstructure developing upon film growth. In all cases a characteristic molecular reorientation from a substrate controlled interface phase towards a bulk-like thick film phase was obtained. On particular surfaces such as Cu(110) even epitaxial film growth was achieved.@footnote 2@@footnote 3@ The studied organic films revealed further a pronounced dewetting which favours the formation of crystalline islands upon deposition. Moreover, the electronic properties of thin pentacene films on various metal surfaces were characterized by UPS. It was found that the magnitude of the interface dipole moment is not directly related to the adsorption energy of the molecules at the metal surface but is caused to some extend by an exchange like coupling mechanism. @FootnoteText@ @footnote 1@ G. Witte and Ch. Wöll, J. Mat. Res. (focuss issue Organic Electronics, 2004).@footnote 2@ S. Lukas et. al., ChemPhysChem 5, 266 (2004).@footnote 3@ S. Söhnchen et al., J.Chem. Phys. in print (2004).

10:40am **OF+EM-WeM8 A Soluble Photopatternable Pentacene Precursor for Use in Thin Film Transistors***,* ***K.P. Weidkamp,*** University of Wisconsin-Madison*; A. Afzali, R.M. Tromp*[1], IBM T.J. Watson Research Center*; R.J. Hamers,* University of Wisconsin-Madison

The practical application of pentacene as an organic semiconductor has been hampered by its lack of solubility in common solvents. Here we report the synthesis and characterization of a photopatternable, soluble pentacene precursor. This precursor, based on an N-sulfinylcarbamate adduct of pentacene, is converted back to pentacene at relatively low temperatures in the presence of acid catalyst and can be patterned by way of chemical amplification in the presence of photoacid generator. After UV illumination, a short, low-temperature post-exposure bake is used to convert the precursor to pentacene and the unexposed area is then

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[1] **Medard W. Welch Award Winner**

washed away with solvent. A very short higher temperature anneal helps to form a crystalline film of pentacene that has mobilities in the range of 10@super -2@ cm@super 2@ V@super -1@ s@super -1@. Features can be patterned as small as 10 µm, small enough for use in many applications such as active matrix displays.

11:00am **OF+EM-WeM9 Electronic Polarization at the Pentacene - Gold Interface*, F. Amy,*** *A. Kahn,* Princeton University

Pentacene has been successfully used as a high-mobility hole transport material. One of the reasons is that the energy of relaxation of the molecular ion is smaller by at least a factor of two than in other commonly used hole transport materials@footnote 1@. However, the full benefit of this relatively high mobility can be realized only if charge carrier injection is not a significant bottleneck in the device. The pentacene/metal interface energetics are therefore of prime importance. We focus here on the specific issue of polarization and narrowing of the transport gap at the pentacene/Au interface. Tsiper et al.@footnote 2@ have shown both experimentally and theoretically for PTCDA/Au that the polarization induced by an electron (P@sub -@) or a hole (P@sub +@) resident on a molecule at the interface increases by ~0.2 eV with respect to the polarization in the bulk of the film. This increase is due to the large polarizability of the metal substrate and results in a narrowing of the transport gap at the interface. This, in turns, affects the modeling of charge injection at interfaces. In this work, we use ultra-violet and inverse photoemission spectroscopy (UPS, IPES) to measure highest occupied and lowest unoccupied molecular orbitals (HOMO, LUMO) of pentacene as a function of film thickness, from one to ten molecular layers. HOMO and LUMO levels represent the hole and electron transport levels, respectively. We find the increase in polarization at the interface to be in line with that measured on PTCDA. @FootnoteText@ @footnote 1@ N.E. Gruhn, et al. J. Am. Chem. Soc., 124, 7918 (2002)@footnote 2@ E.V. Tsiper, Z. Soos, W. Gao and A. Kahn, Chem. Phys. Lett. 360, 47 (2002) .

11:20am **OF+EM-WeM10 Planar Molecular Networks Built by 1D and 2D Polymerization*, M. Stöhr,*** *M. Wahl, M. De Wild,* University of Basel, Switzerland*; C.H. Galka, L.H. Gade,* University of Heidelberg, Germany*; T.A. Jung,* University of Basel and Paul Scherrer Institute, Switzerland*; H.-J. Güntherodt,* University of Basel, Switzerland

Self-assembly of molecules on surfaces directed by different supramolecular interactions has been widely explored. There are striking examples of molecular surface structures, whose formation is driven by metal co-ordination, dipolar coupling or hydrogen bonding. In contrast to these examples, our aim is the formation of covalently linked planar structures by means of polymerization confined in one or two dimensions. The perylene derivative (DPDI) we investigated belongs to a class of compounds which serve as precursors for the production of photovoltaic devices. Recent investigations using differential thermoanalysis and gravimetry demonstrated that bulk DPDI can polymerize releasing ammonia. Inspired by this observation, we tried to exploit the formation of covalent networks on metallic surfaces and to check the feasibility of such an approach for the formation of stable polymer-nanostructures. For this purpose, thin films of DPDI were prepared on Ag(111) and Cu(111) by evaporation in a UHV setup. In a first step, the supramolecular arrangements were analyzed with a home-built STM. A condensed phase with a rectangular unit cell was found on both substrates if the coverage was in the range of 1ML. After annealing to 580K, a rearrangement of the DPDI molecules into a rhombic unit cell structure was observed. This symmetry change was accompanied by the appearance of a link between individual perylene groups which we identify as covalent bonds. Further evidence, in favor of a covalent bond formation is provided by the shortening of the intermolecular distance of the ad-molecular patterns after the thermal activation. We identify these structures as arrays of 1D polymer rows. For lower coverage in the range of 0.3ML only a mobile phase was detected before annealing. However, upon annealing to 580K a stable 2D network with a honeycomb-like structure was observed which conveniently matches the angles and distances expected for the chemically feasible polymer structure.

11:40am **OF+EM-WeM11 UHV-STM/XPS Studies of ACA Molecular Assemblies on Ag(111)*, B. Xu,*** *D. Evans, B. Varughese, J. Reutt-Robey,* University of Maryland

The structures of acridine carboxylic acid (ACA) molecular films grown on Ag (111) by physical vapor deposition were characterized using UHV-STM and XPS. On large terraces (with terrace-spanning diameters exceeding 100 nm), ACA molecules form well ordered 2-d islands. The driving force for island formation is attributed to hydrogen-bond formation between ACA molecules (attractive along [1-10]) and substrate mediated attraction along [11-2]. XPS experiments reveal that H-bond interaction involves the ring nitrogen acting as the H-bond acceptor(O-H...N). On narrow terraces (~3 nm in width) completely different ACA structures are observed. In these confined regions, ACA molecules assemble into dimers, which are further organized into coverage-dependent adlayer structures. Finally, we report the observation of bi-layer and tri-layer structures.

Plasma Science and Technology
Room 213A - Session PS1-WeM
Plasma in Nanoscale Applications

Moderator: W.M. Holber, MKS Instruments

8:40am **PS1-WeM2 Growth, Characterization and Application of Plasma-Assisted Nano-Coatings*, P.P. Joshi,*** *R.V. Pulikollu, S. Higgins, S.M. Mukhopadhyay,* Wright State University

Plasma-assisted coatings have significant application potential as they can be tailored to impart desired properties to the surface. The goal here is to develop a fundamental understanding of the initial stages of growth of these coatings on model flat substrates, and then test the applicability of these on uneven structures. Two types of plasma assisted functional coatings are studied: viz. oxide coatings that imparting surface reactivity (or hydrophilicity) and fluorocarbon coatings that imparting surface inertness (or hydrophobicity). XPS was used for detailed study of chemical composition of the substrate and coating atoms at various stages of deposition. Atomic force microscopy was used to study the morphology of these coatings as they grow. Combined XPS and AFM results for both the coatings rule out any possibility of the patchy coatings with exposed substrate (complete coverage of substrate), and also indicate that these coatings are effective on nanometer scale. These studies show that plasma-assisted chemical deposition can be a very viable approach to creating functional nano-coatings on surfaces of nano-structured solids. Initial studies on single-crystal silicon were followed up with comparative studies on different types of substrates (sapphire, graphite etc.). The effectiveness of these coatings on uneven surfaces such as composite core structures and fibrous films will be discussed.

9:00am **PS1-WeM3 Plasmas Technologies in Microfluidics for Novel Bioanalytical Systems*, T. Ichiki,*** Toyo University, Japan **INVITED**

Development of innovative nano-bio-analytical systems is coming to reality by the combination of the microfluidic device technologies and the precise image processing systems using an optical microscope or a scanning probe microscope. Highly functional microfluidic devices can be fabricated by the application of advanced nano/microfabrication technologies developed in the ULSI industry. Microfluidic devices under development in our projects are expected to enable direct manipulation and analysis of each single cell and obtain molecular-level information about life phenomena of the cell, which has not been attainable by the conventional analysis tools. Recent progress and the future scope in plasma processing for microfluidic devices will be presented in this paper.

9:40am **PS1-WeM5 Fabrication of 7nm High Aspect Ratio Nanocolumns by Low Energy Neutral Beam Etching using Ferritin Iron-Core Mask*, T. Baba,*** *T. Kubota,* Tohoku University, Japan*; Y. Uraoka, T. Fuyuki,* Nara Institute of Science and Technology, Japan*; I. Yamashita,* Matsushita Electric Industrial Co., Ltd., Japan*; S. Samukawa,* Tohoku University, Japan

The critical dimension of semiconductor devices is continuously expected to be decreased up to less than 50 nm within the next decade. However, the conventional lithography has a theoretical limit to define patterns smaller than wavelength of light. In this study, we report a new method to fabricate nanometer-scale structure by using biomaterial etching mask and a newly developed neutral beam etcher. A large number of atomically equal molecules can be easily produced due to the nature of biomaterials, such as proteins, that are synthesized based on the DNA information. Ferritin is a type of proteins, which is capable of biomineralization to make inorganic materials. It can biomineralize iron-core as hydrated iron oxide. By using the iron-core as an etching mask, we fabricated a number of 7nm nanocolumns in their diameters. Neutral beam etcher has been employed in this experiment. Neutral beams could realize accurate and damage-free etching because it could prevent charged particles and ultraviolet photons. Employing the uniform iron-core mask and neutral beam etching, high aspect ratio nanocolumn structure was successfully fabricated, and almost vertical sidewalls profiles were able to be achieved. The aspect ratio of 6.57 was achieved with 7 nm of the diameter, which was identical to that of the iron core. The neutral beam enabled damage-free etching and led to an accurate transfer from the iron-core to the silicon substrate without any aggregation of the iron-cores.

10:00am **PS1-WeM6 Deposition of Nanocomposite Layers for Ultralow Dielectric Applications***, **G.R. Alcott,*** TNO-TPD, The Netherlands*; M. Creatore,* Eindhoven University of Technology, The Netherlands*; J. Linden,* TNO-TPD, The Netherlands*; M.C.M. van de Sanden,* Eindhoven University of Technology, The Netherlands

As the dimensions of integrated circuit devices scale to smaller feature sizes, the resistance-capacitance (RC) delay of the metal interconnect will increasingly limit the performance of high speed logic chips. The integration of ultralow dielectric materials (k < 2.5) can reduce this problem and the use of the porous materials is now deemed necessary if the future targets of chip design are to be achieved [@footnote1@]. While many candidates for ultralow-k applications exist, many of the most promising are synthesized using wet chemical processes involving harmful solvents and multiple process steps. In this work a novel dual plasma reactor is used to simultaneously synthesize and incorporate porous nanometre sized particles into SiO@x@C@y@H@z@ layers. Porous nanoparticles and siloxane layers are synthesized from a TEOS/O@2@ and 1,2-bis(trimethyl)siloxyethane precursors respectively. Structure and composition of the nanocomposite layer produced are characterised using ESEM and infrared absorption spectroscopy. Thermal stability and electrical properties are determined to evaluate the thin films suitability in low-k dielectric applications. Dielectric constants as low as 1.82 ± 0.02 were achieved at 1 MHz. @FootnoteText@ @footnote1@ http://public.itrs.net.

10:20am **PS1-WeM7 Nano-Scale Pattern Transferring By Plasma Etching***, **Y. Zhang**, C. Black, K. Guarini, T.J. Dalton,* IBM T. J. Watson Research Center **INVITED**

Patterning challenges for the 22nm node and beyond in the ITRS roadmap requires precision etching of semiconductor nano-scale features at the sub-10nm regime. In this paper, we report the recent results of patterning true nano-scale features using plasma etching. A newly established method called "nanometer-scale pattern registration and alignment by directed diblock copolymer self assembly" was employed. Using this technique, large-scale (across 200 mm wafers) high-density (> 10E6/cm2) nano-scale features were produced; both holes and line arrays with 40nm pitch were fabricated. These structures are beyond any state-of-art conventional optical lithography and e-beam writing technologies. The nanometer holes & line arrays were used to study plasma etching characteristics and challenges for different materials (silicon, silicon dioxide, and silicon nitride) with different plasma chemistries (fluorine-, chlorine-, and bromine-based). Besides scaling of the feature size or critical dimension, the thickness of the film stacks to be etched were also scaled. The patterning of nano-scale line arrays was more challenging that the patterning of nano-scale hole arrays when using ultra-thin and ultra-narrow diblock polymer masks. Among the challenges for line arrays were: (1) deformation of the polymer masks (due to poor thermal conductivity and film stress); (2) depth limitations due to selectivity to the mask; and (3) line edge roughness, (LER). These challenges have not only made the pattern transferring more difficult (even with current state-of-art plasma etching tools), but also indicate that plasma etching may be approaching a limits as it is currently implemented. A few proposed limiting factors of current etching tooling, underlying principles of different chemistries, and processing parameters and their advantage and drawback to etching nanometer scale features will also be discussed.

11:00am **PS1-WeM9 Crucial Role of Side Wall Deposition during Synthesis of Spatially Separated Vertically Aligned Carbon Nanofibers by C-PECVD***, **A.V. Melechko**,* University of Tennessee, Knoxville*; D.K. Hensley,* Oak Ridge National Laboratory*; X. Yang, K.L. Klein,* University of Tennessee, Knoxville*; H.M. Meyer, D.H. Lowndes,* Oak Ridge National Laboratory*; M.L. Simpson,* Oak Ridge National Laboratory, University of Tennessee

Catalytic plasma enhanced chemical vapor deposition (C-PECVD) is used for deterministic synthesis of vertically aligned carbon nanofibers(VACNFs). In this process the location, orientation, diameter and length of the fiber can be controlled. Deterministic synthesis is extremely important for incorporation of nanofibers into devices with nanoscale elements such as microfabricated electron field emission sources, gene delivery arrays, intracellular electrochemical probes, scanning probe microscopy tips etc. In C-PECVD the formation of the carbon nanofiber via the catalytic particle is accompanied by the non-catalytic deposition of an amorphous carbon film over the surface. In order to prevent the undesirable film formation carbon source gas is diluted with etchant gases and the reactor is operated in an etching rather than deposition regime. The operating parameters usually are tuned so that the removal rate of carbon film is exactly equal to its deposition rate so that the growing nanofiber is not damaged. This is especially important for isolated nanofibers as their sidewalls are completely exposed. Such a balance is difficult to maintain over large-scale substrates with non-uniform patterns. We will report on a new regime in which Si from the substrate participates in the formation of a protective coating on the nanofiber sidewalls. In this process the formation of a carbon film is completely eliminated and the functionality of the VACNF is not affected. The results of SEM, EDX and AES with spatial resolution were used to determine the atomic composition and structure of coated carbon nanofibers. The dependence of side wall deposition on the plasma power, gas flow ratio and pressure will be discussed. In addition, a solution for non-silicon substrates will be offered.

11:20am **PS1-WeM10 Catalytic Plasma Enhanced Chemical Vapor Deposition of Ultrasharp Vertically Aligned Silicon Nanocones and Their Characterization***, **K.L. Klein**, A.V. Melechko,* University of Tennessee/ORNL*; P.D. Rack,* University of Tennessee*; D.K. Hensley,* Oak Ridge National Lab*; J.D. Fowlkes,* University of Tennessee*; H.M. Meyer III, L.F. Allard, D.H. Lowndes,* Oak Ridge National Lab*; M.L. Simpson,* University of Tennessee/ORNL

We present a new method for the synthesis of vertically aligned ultrasharp silicon nanostructures with tip diameters as small as 10 nm. Silicon nanocones were produced using dc plasma-enhanced chemical vapor deposition (dc-PECVD) using the Si substrate as a sole source of Si and thin film Cu or Au as a catalyst. High resolution SEM, TEM, EDX, STEM, and AES were utilized to determine the microstructure and composition of the nanocones. We have explored variations in the structure and growth mode of these nanocones with respect to growth conditions. This structure will be described in detail and a growth mechanism proposed. The similarities and differences of this new growth process as compared to standard SiH4-based VLS growth will be discussed. Finally, we will describe their potential use in applications such as gene delivery arrays and field emission cathodes.

11:40am **PS1-WeM11 Gas-Phase Synthesis of Single-Walled Carbon Nanotubes by Hot-Filament-Assisted Plasma Chemical Vapor Deposition and Its Analysis by Mass Spectroscopy***, **Y. Hayashi**, Y. Morimoto, Y. Kogawara, S. Nishino,* Kyoto Institute of Technology, Japan

Single-Walled Carbon Nanotubes (SWNTs) have been successfully synthesized in gas phase by Hot-Filament-Assisted Plasma Chemical Vapor Deposition. Hot filaments were used for heating a reaction zone and for the assistance of generation and stabilization of DC plasma. Ethylene diluted 30 % in hydrogen was flowed through a pipe into a stainless chamber to the direction of the hot filaments. The vapor of ferrocene was included into the reaction gas before introduction to the chamber. Three tungsten wires were stretched and they were heated 1800-2000 °C. The pressure in the chamber was maintained 3.33 kPa (25 Torr). At 25 mm downstream of gas flow from the hot filaments, a cupper plate was placed perpendicular to the flow. DC voltage of +300 V with the current of 150 mA was applied to the cupper plate with the hot filaments and the chamber grounded. Glow discharge plasma was generated between the hot filaments and the cupper plate for about one hour. Carbon fine particles collected on the plate as well as on another plate put under the plasma on the bottom of the chamber were evaluated by Raman spectroscopy and they were confirmed to be SWNTs. The diameter of the SWNTs were observed by transmission electron microscopy to be 1 to 2 nm. The fact that more SWNTs were obtained on the bottom plate than on the downstream plate suggests their synthesis in gas phase. Quadrupole mass spectrometry was carried out for the analysis of molecules during the synthesis. The evolution of partial pressure of benzene corresponded well with the evaporation of ferrocene while that of iron did not. The results support that iron clusters were formed in gas phase through the decomposition of ferrocene and that large amount of SWNTs were grown on them being suspended in the glow discharge plasma for a long time.

Plasma Science and Technology
Room 213B - Session PS2-WeM

Plasma Sources

Moderator: J. Caughman, Oak Ridge National Laboratory

8:20am **PS2-WeM1 Langmuir Probe Measurements of Change in Plasma Parameters with Change in Chamber Geometry in Electronegative Plasmas***, **S.P. Sant**, E.A. Joseph, B.S. Zhou, L.J. Overzet, M.J. Goeckner,* University of Texas at Dallas

The affect of chamber geometry on the characteristic behavior of two electronegative gases commonly used in the processing industry, namely CF@sub 4@ and O@sub 2@ were studied. The chamber used is the modified Gaseous Electronics Conference (mGEC) reference cell. The mGEC was designed to allow rapid changes to its geometrical structure and wall materials, allowing us to closely inspect various plasma-wall interactions. A Langmuir probe was used to obtain axial and radial measurements of ion density, electron density, plasma potential, electron temperature and floating potentials. These parameters were measured for a combination of two different source â?" chuck gaps (4 cm and 9.8 cm) and chamber diameters (20 cm and 64 cm). It is observed for both gases, that the electron temperature ranges from ~ 5 eV to ~ 1 eV as we move from the center towards the walls in the 64 cm diameter case with the narrow gap. For wider gap the peak temperatures are ~ 30% lower for O@sub 2@ case only, while they remain approximately the same for CF@sub 4@. In comparison, the plasma density drops by a factor of 2 in the center (1.5 E 11 to 0.8 E 11) with decrease in gap, but the center density remains fairly constant independent of chamber diameter. In general, it is observed that the experimental values vary with change in gap (coil to chuck distance), but remain fairly constant with change in chamber diameter. This work is supported by a grant from NSF/DOE, CTS â?" 0078669.

8:40am **PS2-WeM2 Modeling of a Commercial Dual Frequency Magnetically Enhanced Capacitively Coupled Plasma Reactor with Rotating Static Magnetic Field***, **T. Panagopoulos**,* Applied Materials, Inc.*; A.M. Paterson, J.P. Holland,* Applied Materials Inc.

Magnetically enhanced reactive ion etching (MERIE) reactors have recently been modeled for 200mm wafer processing chambers with single frequency and uniform static magnetic field. An extension of this work is presented for a commercial 300mm dual frequency MERIE reactor with rotating static magnetic field for an argon discharge. The magnetic field is modeled in the 3D space (CFD-ACE) and it is used as an input in a 2D computational model (HPEM). The different moments of the static magnetic field are solved independently and the species spatial profiles are compared for different magnetic field intensities and operating pressures. The use of magnetic field results in more confinement of the ion density within the area of the two electrodes. This confinement is more effective for lower pressures (10s of mTorrs) and tends to confine the plasma at the wafer center. On the other hand, when the pressure increases to a few hundreds of mTorrs, the plasma density is confined close to wafer edge. The density profiles are affected by the time averaged ionization source by bulk electrons. When no magnetic field is applied in the chamber, the ionization source is located near the wafer edge and in the middle of the inter-electrode spacing. As the magnetic field increases in a high pressure regime, the ionization sources move closer to the bottom electrode, and for even higher magnetic field (~100G) most of the ionization takes place at the edge of the bottom electrode with a lessened contribution from the top electrode. For lower operating pressures (~30 mTorr), the ionization patterns are different with a substantial contribution from the top electrode and bulk of the plasma, for average magnetic fields. In a similar way the dc bias is affected by the operating pressure regime; it becomes less negative as the magnetic field increases at low pressures, while it becomes more negative for the high pressure regime. Experimental wafer results agree with the simulation trends.

9:00am **PS2-WeM3 Control of Uniformity in Multifrequency Capacitively Coupled Plasmas Considering Edge Effects@footnote 1@***, **J. Lu**, M.J. Kushner,* University of Illinois at Urbana-Champaign

Multifrequency capacitively coupled plasmas are finding increasing use in etching and deposition applications. The optimization of ion flux uniformity is known to be a sensitive function of the edge electrical boundary condition embodied in the shape, permittivity and conductivity of the guard (or focus) ring. To investigate these geometrical and electrical effects, a 2-dimensional plasma hydrodynamics model has been developed which uses an unstructured numerical mesh. This meshing capability enables fine resolution of the substrate structures. The dependence of the ion flux uniformity on the electrical boundary condition using single and dual frequency operation (10s MHz and a few MHz with frequencies on one electrode or separate electrodes) will be discussed for process conditions of 10s mTorr in electropositive (Ar) and electronegative (Ar/fluorocarbon, Ar/O@sub 2@) mixtures. @FootnoteText@ @footnote 1@ Work supported by SRC and NSF.

9:20am **PS2-WeM4 Potentials and Fields in a 300-mm Dual-Frequency Capacitively Coupled Plasma Reactor***, **P.A. Miller**, E.V. Barnat, G.A. Hebner,* Sandia National Laboratories*; A.M. Paterson, J.P. Holland, T. Lill,* Applied Materials

Dual-frequency capacitively coupled plasma reactors provide separate control over plasma generation and ion extraction. Usually, a vhf power supply (source) is used to generate and sustain the plasma and an hf power supply (bias) is used to extract ions. At present there is debate over the optimum choices for the two operating frequencies, and whether they should be applied to one or two electrodes. Higher frequencies facilitate plasma generation with mild and controllable dissociation of feed-gas molecules, but the attendant shorter wavelengths cause concern over spatial variations in plasma properties. Regardless of frequency choices, electrical nonlinearity of plasma sheaths causes harmonic generation and mixing of source and bias frequencies. These processes, and the resulting spectrum of frequencies, are as much dependent on electrical characteristics of matching networks as on the plasma sheath properties. We investigated such electrical effects in a 300-mm Applied-Materials plasma reactor. Data were taken for 13.56-MHz bias frequency (chuck) and for source frequencies from 30 to 160 MHz (upper electrode). An rf-magnetic-field probe (B-dot loop) was used to measure the radial variation of fields inside the plasma. We will describe the results of this work. This work was supported by Applied Materials 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.

9:40am **PS2-WeM5 Time and Position Resolved Characterization of ICP and Double-ICP Sources***, **P. Awakowicz**,* Ruhr-Universität Bochum, Germany **INVITED**

Inductively coupled rf sources are important tools in semiconductor plasma processing. In recent years, these tools also have been investigated for medical applications like plasma sterilisation and surface modification of polymers. This is the reason why a double ICP source has been developed. In order to characterize these different plasma sources, Langmuir probe measurements, energy-resolved mass spectrometry, optical emission spectroscopy and plasma modelling have been applied to different ICP sources. For time resolved measurements, Langmuir probe and mass spectrometer were synchronized. Time and position dependent profiles provide a deeper insight into physics of these source and provide additional parameters like puls frequency and duty cycle for adjusting new or improved processes.

10:20am **PS2-WeM7 Comparison of Fluorocarbon Gases and NF3 for Plasma Chamber Cleaning with Transformer-Coupled, Toroidal Source***, **B. Bai**, H.H. Sawin,* Massachusetts Institute of Technology*; L. Gary, M. Mocella,* DuPont Electronic Gases

In recent years, remote chamber cleaning has begun to replace in situ chamber cleaning for Chemical Vapor Deposition (CVD), due to the lower occurrence of chamber wall erosion and lower perfluorocompound (PFC) gas emission. We have tested a high-power transformer-coupled toroidal plasma source typically used with NF3 to produce fluorine atoms for chamber cleaning. The ASTRONex unit couples high power levels (<10 kW) into the feed gases, leading to high neutral temperatures (as high as 6000K) under conditions that produce relatively low electron temperatures. These condition produce very high degrees of dissociation of not only NF3, but also for fluorocarbon compounds â?" contrary to what has been seen in lower power and/or microwave units for remote chamber cleaning. In this work, a systematic comparison has been made among various fluorocarbon compounds (with added O2) including CF4, C2F6, C3F8, and C4F8, along with NF3. Trends in cleaning rates, which are significantly different from earlier studies in other units, will be described. Tool emission studies with Fourier Transformed Infrared Spectroscopy (FTIR), along with analysis of the cleaned surfaces via X-ray Photoelectron Spectroscopy (XPS) and Atomic Force Microscopy (AFM), will also be presented. Plasma parameters were also measured to better understand the kinetics in the source. Neutral gas temperatures were obtained by fitting rovibrational bands of diatomic species like CO, CF or added N2. Electron temperature and electron density were determined by the atomic argon spectrum, while the atomic concentrations of fluorine and oxygen species in the plasma source were measured by advanced actinometry. For these two optical emission spectroscopy measurements, a full consideration of optical cascading and radiation trapping was necessary due to the high source pressure (~1 torr).

10:40am **PS2-WeM8 Scaling of Low-pressure Ionized Metal PVD Reactors@footnote 1@***, **V. Vyas**, M.J. Kushner,* University of Illinois at Urbana-Champaign

Ionized metal physical vapor deposition (IMPVD) at sub-mTorr pressures is used to deposit diffusion barriers and seed layers onto high aspect ratio trenches. At these pressures, conventional fluid or hybrid simulations are of questionable validity as transport is highly non-equilibrium and a kinetic approach may be warranted. In this work, a Monte Carlo simulation for ion and neutral transport (IMCS) has been developed and integrated into a 2-dimensional plasma equipment model to improve our capabilities to address lower pressures. The ion velocity distributions obtained from the IMCS are used to obtain transport coefficients for use in heavy particle momentum and energy conservation equations, thereby extending their validity to lower pressures. Hollow Cathode Magnetron (HCM) plasma sources for Cu deposition have been investigated using the model while varying power, pressure and source geometry. The consequences of varying these parameters on the uniformity of reactant fluxes, and their energy and angular distributions on the substrate will be reported. Comparisons will be made to experiments for plasma properties and deposition profiles. @FootnoteText@ @footnote 1@ Work supported by SRC and NSF.

11:00am **PS2-WeM9 Production of Meter-scale High-density Microwave Plasmas for Giant Materials Processing***, **H. Sugai**, Y. Nojiri, T. Ishijima, E. Stamate,* Nagoya University, Japan

There has been a great need for meter-scale high-density plasma sources for manufacturing giant microelectronics devices such as liquid crystal display and solar cell. Capacitive discharges at frequencies in VHF range enable us to generate a medium-density meter-size plasma, however standing wave effect and edge effect significantly degrade the plasma uniformity. Here, we present a new technology for production of large-area uniform high-density plasmas based on surface wave excitation at 2.45 GHz. The critical challenges are (1) how to avoid huge atmospheric pressure acting on a dielectric window for microwave radiation, and (2) how to design an antenna-plasma coupling so as to attain the plasma uniformity over meter-size. The first issue is dodged by employment of a dielectric-filled waveguide and slot antennas, which are contained in a low-pressure plasma vessel. The second issue is solved by a careful design of slot antenna and by introduction of corrugated dielectric surface. Surface waves propagating along the interface between a dielectric plate and plasma are investigated in an analytical model and also in FDT simulation. The standing modes of surface waves at 2.45 GHz were successfully detected by a movable antenna, and the mode numbers are in good agreement with the wave theory. In the preliminary experiments using a large discharge vessel (length 1 m, width 0.3 m), we obtained the plasma density of ~5x10@super11@ cm@super-3@ with ~10 % uniformity at 2.5 kW in argon at 50 mTorr.

11:20am **PS2-WeM10 Extraction of a Directional Ion Beam with Controlled Energy Using a Pulsed Plasma***, **L. Xu**, V.M. Donnelly, D.J. Economou,* University of Houston

A 13.56MHz pulsed (typically 50µs ON/50µs OFF), capacitively coupled plasma reactor was developed to generate a nearly monoenergetic, directional ion beam. The DC bias on the target ranged from -150 to -270 volts depending on the input power and pressure. A Langmuir probe was employed to characterize the pulsed Ar plasma and a 3-grid ion energy analyzer was used to measure the ion energy distribution (IED). The EEDF during the power-ON fraction of the cycle was non-Maxwellian with a high energy tail, most likely due to secondary electrons emitted from the target. Beyond 4 µs into the power-OFF period, a Maxwellian EEDF was observed and the electron temperature (T@sub e@) decayed rapidly. The evolution of the EEDF during the power-OFF period was also used to verify the collapse of T@sub e@. After a specified delay in the power-OFF period, a positive voltage pulse was applied to a DC ring electrode surrounding the plasma to raise the plasma potential (V@sub p@) and "push" positive ions through a grounded grid out of the plasma. With the DC ring electrode voltage pulse on, a high-voltage shift of a Langmuir probe IV curve signified an increase of V@sub p@. With 50 V applied to the DC ring, the energy of the extracted ion beam peaked at 49.4 V, while the FWHM of the IED was 4.3 V, limited by the rise time of the homemade voltage pulse circuit. The ion beam is also expected to be very directional since the ion temperature depends on T@sub e@, which was very low during ion extraction. Finally, the sheath thickness during ion extraction was much larger than the holes of the grid, resulting in a vertical sheath electric field and minimal divergence of the ions as they traversed the grid holes. This was verified by a self-consistent PIC simulation. Work supported by NSF.

11:40am **PS2-WeM11 Particle-in-Cell Simulation of Ion Extraction Through a Grid***, **S.K. Nam**, V.M. Donnelly, D.J. Economou,* University of Houston

Ion extraction from a plasma through a grid finds applications in ion beam and neutral beam sources. The flux, energy and angular distributions of ions (or neutrals) extracted from the plasma are of primary importance in such applications. These quantities depend critically on the shape of the meniscus (plasma-sheath boundary) formed over the surface topography of the extraction grid. For example, when the sheath thickness is comparable to or smaller than the grid hole size, the sheath tends to conform to the surface topography of the grid (plasma molding) resulting in divergent beams. A self-consistent Particle-in-Cell (PIC) simulation of ion extraction from a plasma through a grid was developed. Emphasis was placed on extracting ions, which are as mono-energetic and as directional as possible. The effect of control parameters affecting the sheath thickness (plasma density, electron temperature, sheath potential) relative to the grid hole size (and aspect ratio) was studied. For a hole size of 0.5 mm, the FWHM of the ion angular spread was about 4, 10, and 20 degrees for sheath thickness of 4.3, 2.6, and 0.7 mm, respectively (sheath potential of 50 V, electron temperature 3 eV). Ion flux uniformity was very high for the thick sheath case (within a 3%) but degraded gradually for the thinner sheaths due to stronger ion divergence. Conditions which allowed the extraction of an ion beam with specified energy and angular spread were determined. The influence of hole-hole interaction was also studied. Work supported by the National Science Foundation.

Surface Science
Room 210B - Session SS1-WeM
Metal Oxides and Clusters I: Formation and Structure

Moderator: B.D. Kay, Pacific Northwest National Laboratory

8:20am **SS1-WeM1 The Chemistry of Au Clusters Supported on Titania: Early Steps Towards Understanding the Mechanism of Propene Epoxidation***, G. Mills, S. Chretian, V. Shapovalov, **H. Metiu**,* University of California, Santa Barbara **INVITED**

We use density functional calculations to try to increase our understanding of the interactions of hydrogen, oxygen, propene, and propene oxide with gold clusters in gas phase, with titania, and with gold clusters supported on titania. Our goal is to clarify the mechanism of propene epoxidation. I will also report briefly on a collaboration with Martin Moskovits concerning the modification of catalytic activity of CO oxidation, by manipulating the electron density in tin oxide nanowires.

9:00am **SS1-WeM3 Surface and Subsurface Oxidation of Ni(100) and Ni(111) Studied by Medium Energy Ion Scattering***, **M.A. Muñoz-Márquez**,* University of Warwick, UK, United Kingdom*; R.E. Tanner, D.P. Woodruff,* University of Warwick, UK

Using medium energy ion scattering (MEIS) and specifically 100 keV H@super +@ incident ions, the oxidation of the Ni(100) and Ni(111) surfaces have been investigated at temperatures around 200-300°C and with oxygen exposures up to 6000 L. This treatment range corresponds to that typically used to produce well-defined NiO(100) surfaces on Ni(100) and involves significantly thicker oxide formation than has been investigated by conventional surface science techniques in the past. The potential of MEIS to probe the deeper subsurface is highly relevant in these studies, as oxide formation >100 Å is seen on Ni(111). While it is well-established that the earliest stages of oxidation occur at lower exposures on Ni(111) than Ni(100), attributed to site blocking in the different chemisorbed oxygen phases on the two surfaces, our results show that this greater reactivity of Ni(111) persists to rather deep oxidation. Throughout these oxide films the stoichiometry of NiO is retained. Through the use of 'double-alignment' scattering geometries and qualitative LEED, the crystallography of these oxide layers has been investigated. LEED shows that on Ni(111) two (of the possible three) orientational domains of NiO(100) form, attributed to a slight misorientation of the surface. In general, the average crystalline registry with the bulk is poor, although at intermediate exposures a surprising result is that the outermost layers appear better-ordered than the near sub-surface. This is attributed to the probable influence of thick islands of limited lateral extent which causes the more penetrating ions to pass through differently oriented oxide islands. On Ni(111) simulations using the VEGAS code confirm that the data are consistent with this rationale. On Ni(100), the apparent poor order can also be reproduced in simulations assuming the NiO(100) crystallites are tilted on the surface as previously proposed on the basis of SPA-LEED investigations.

9:20am **SS1-WeM4 Thermodynamics of Pd(111) Oxidation from 10@super -7@ to 25 Pa: An In-Situ Photoemission Study***, **D.F. Ogletree**, G. Ketteler, H. Liu, E.L.D. Hebenstreit, H. Bluhm, M. Salmeron,* Lawrence Berkeley National Laboratory

The oxidation of Pd(111) has been studied in equilibrium with oxygen gas between 10@super -7@ and 25 Pa over a temperature range of 300 to 925 K. The experiments were carried out in a newly commissioned, second-generation high pressure photoemission spectroscopy (HPPES) system operating at the Molecular Environmental Sciences synchrotron beamline@footnote 1@. After UHV sample cleaning, the Pd(111) crystal was transferred to a variable pressure experimental cell coupled to a differentially pumped electron spectrometer. High resolution photoemission spectra were recorded for the Pd 3d@sub 5/2@, O1s/Pd3p@sub 1/2@ and valence band regions at different combinations of oxygen pressure and sample temperature. Dynamic and reversible changes in surface oxidation were observed in response to changes in the thermodynamic environment of the palladium substrate. An analysis of the thermodynamics and kinetics of the palladium-oxygen system will be presented. @FootnoteText@ @footnote 1@ Beamline 11.0.2 at the LBNL Advanced Light Source, Berkeley, CA USA.

9:40am **SS1-WeM5 Oxidation of Pt(111) by Gas-Phase Oxygen Atoms***, **J.F. Weaver**, A.L. Gerrard, J.J. Chen,* University of Florida

The oxidation of Pt(111) by an atomic oxygen beam has been investigated as a function of surface temperature using temperature programmed desorption (TPD), X-ray photoelectron spectroscopy (XPS) and electron energy loss spectroscopy (ELS). For oxygen coverages below about 0.50 ML (where 1 ML = 1.5 x 10@super 15@cm@super -2@), the rate of atomic oxygen adsorption is found to be insensitive to surface temperature over the range from 150 to 450 K. After 0.5 ML of atomic oxygen is adsorbed, the oxidation rate decreases with decreasing temperature, and the oxygen coverage saturates at values that also decrease with decreasing temperature. At the highest temperature investigated (450 K), the oxygen coverage at saturation is about 2 ML, whereas only 0.25 ML can be generated by dissociatively adsorbing O@sub 2@ on Pt(111) in ultrahigh vacuum. The mechanism for Pt(111) oxidation involves the initial formation of a chemisorbed layer, within which the oxygen atoms experience significant repulsive interactions after the coverage is increased above 0.25 ML. Long-range order in the high-coverage adsorbed layer could not be observed with LEED. At each surface temperature investigated, islands of platinum oxide begin to form after the oxygen coverage exceeds about 0.5 ML. TPD and ELS data suggest that the oxide islands grow three-dimensionally at surface temperatures ranging from 150 to 450 K, and that their formation is accompanied by the regeneration of metallic regions on which additional oxygen adsorbs and subsequently incorporates into growing islands. The kinetics of the oxidation process and the reactivity of the surface oxygen phases will also be discussed.

10:00am **SS1-WeM6 Thermodynamically Controlled Self-Assembly of Oxide Nanostructures@footnote *@***, **F.P. Netzer**, J. Schoiswohl, M Sock,* University of Graz, Austria*; G. Kresse,* University of Vienna, Austria*; S. Surnev, M.G. Ramsey,* University of Graz, Austria

The fabrication of surface-supported nanoscale oxide materials in low dimensions via a chemically driven self-assembly process of novel oxide cluster molecules is reported. As opposed to usual molecular self-assembly, where the construction units are deposited directly from the gas phase, the oxide building blocks with a unique stoichiometry and structure form spontaneously on a Rh(111) metal surface. These can be organised into different two-dimensional oxide structures by careful adjustment of the chemical potential of oxygen µ@subO@, allowing the controlled design of oxide nanostructures on a metal surface. This is demonstrated by following, at the atomic level, the formation and aggregation of planar vanadium oxide V@sub6@O@sub12@ clusters. The planar V@sub6@O@sub12@ cluster molecules form under appropriate conditions of µ@subO@ and of the vanadium concentration at the Rh(111) surface. The structure and stability of these hexagonal V@sub6@O@sub12@ clusters have been elucidated by STM and density functional theory (DFT) calculations. The V@sub6@O@sub12@ structures do not exist in the gas phase and constitute a novel kind of cluster material, that is stabilised by the metal-cluster interface. The V-oxide clusters are mobile at elevated temperature and their surface diffusion has been studied in variable-temperature STM experiments: the diffusion parameters indicate diffusion of the entire clusters. The V@sub6@O@sub12@ units can be organised by self-assembly into different 2D oxide structures, depending on µ@subO@. The assembly process occurs via a reductive or oxidative condensation process, which involves strong chemical bonding interactions with partly covalent and ionic character. Nevertheless, the here reported aggregation is reversible, and by adjustment of µ@subO@ and the Rh surface temperature the V@sub6@O@sub12@ clusters can be regenerated from the oxide islands by 2D re-evaporation. @FootnoteText@ @footnote *@ Work supported by the Austrian Science Funds.

10:20am **SS1-WeM7 STM/AFM Study of WO@sub 3@ Cluster Growth on Highly-Oriented Pyrolitic Graphite***, **O. 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

With the ultimate goal of understanding the catalytically activity of WO@sub 3@ clusters supported on oxide surfaces, we have investigated WO@sub 3@ deposition on highly-oriented pyrolitic graphite (HOPG) using in-situ scanning probes. Our efforts were aimed at understanding how the WO@sub 3@ cluster size and morphology depend on deposited amount and substrate temperature. In this work we have studied tungsten oxide films grown on HOPG substrate at temperatures ranging from 300 to 650 K and having thickness from submonolayer up to ~1 µm. STM images of WO@sub 3@clusters formed from submonolayer WO@sub 3@ deposition at room temperature show fractal-like shape. This shape suggests that a diffusion-limited aggregation mechanism governs the growth. Scanning tunneling spectroscopy indicates that the WO@sub 3@ clusters are semiconducting in nature. Tip induced effect leading to complete removal of WO@sub 3@ clusters from HOPG are observed upon extended scanning. In contrast, non-contact AFM imaging does not does not perturb the WO@sub 3@clusters. Possible mechanisms of the tip induced removal of WO@sub 3@ on HOPG will be discussed. Deposition of a submonolayer amount of WO@sub 3@ at ~ 600 K leads to the formation of WO@sub 3@ needle like crystallites of relatively uniform width (~15-20 nm) and length (~100-300 nm). The crystallites are mostly attached to the steps indicating that steps are the preferred nucleation centers. The needle-like growth of WO@sub 3@ crystallites persists even for thicker deposits (~ 1 µm). Ex-situ X-ray diffraction (XRD) analysis performed on thick films suggests that the WO@sub 3@ crystals have cubic symmetry. @FootnoteText@ Pacific Northwest National Laboratory is operated for the Department of Energy by Battelle under Contract DE-AC06-76RLO 1830.

10:40am **SS1-WeM8 Surface and Interface Analysis of MgxZn1-xO for Cubic, Hexagonal and Intermediate Phases by X-Ray Photoelectron and Rutherford Back Scattering Spectroscopies***, S. Hullavarad,* University of Maryland*; R. Vispute,* Bluewave Semiconductors, Inc.*; S. Dhar, T. Venkatesan, **I. Takeuchi**,* University of Maryland

MgZnO has attracted increased attention for its unique properties of existence in multiphases either in hexagonal for 0<Mg<0.35 or cubic for 0.35<Mg<1 in MgxZn1-xO. This material is of significant importance for various applications in flame sensors, UV index monitors and missile plume detection. The presence of Mg with a composition of 0-100% in ZnO lead to higher bandgaps ranging from 3.6eV to 7.8 eV of resulting MgZnO. This allows picking up desired Mg composition corresponding to suitable UV sensitive window and growing on lattice matched substrate. In this study we have picked up three Mg compositions representing hexagonal, cubic and intermediate regions. The samples are characterized by X-Ray Diffraction, Rutherford Back Scattering techniques for crystalline quality, and composition of the films. UV-Visible spectroscopy is used for analyzing the optical property of MgZnO films. In this work we emphasize the role of surface and interface in quality of material from crystal structure, grain boundary related defects and the cumulative effect on devices fabricated on such materials by surface sensitive study carried out using X-Ray Photoelectron and interface study by Rutherford Back Scattering spectroscopy.

11:00am **SS1-WeM9 Novel Stages of Growth of Metal Oxide Nanodots: Cu2O on SrTiO3(100)@footnote 1@***, **I. Lyubinetsky**, A.A. El-Azab, A.S. Lea, S.T. Thevuthasan, D.R. Baer,* Pacific Northwest National Laboratory

Although similar to semiconductor nanostructures in some ways, oxide nanodots have been observed in greater structural variations. Here we report on a significant difference in the growth process which exhibits novel stages. Self-assembled formation of the crystalline cuprous oxide (Cu2O) nanodots on the SrTiO3(100) substrate has been carried out using oxygen plasma assisted MBE and evaluated by XPS, AES, XRD and AFM. Selective formation of the nanodots of single Cu2O-phase occurs only in a very narrow growth parameter window, in comparison with the bulk phase diagram. Formation of Cu2O nanoclusters (with the size range of 10-50 nm) may be described as progressing through several stages. Unlike lattice-mismatched heteroepitaxy in the majority of semiconductor systems, initial stages of the growth of oxide nanodots proceed without formation of the wetting layer. Already at sub-monolayer coverages, small, truncated square Cu2O dots start to form. At next, novel stage a continued deposition leads to increase of the dot density, not the size, and results in reaching a critical dot density, upon which larger nanoclusters start to grow. Resulting morphology consists of large islands on top of the closed-packed layer of the small nanodots. Using a kinetic model of film morphology development, we show that the larger island formation can be caused by small dot coalescence, driven by fluctuation of island-island separation at increased dot density. Under different surface conditions of the SrTiO3(100) substrate (high temperature annealed, perfect TiO2-terminated surface vs. original mixed-terminated surface) significant differences in the uniformity of the nanodot distribution have been observed. @FootnoteText@ @footnote 1@ This work was jointly supported by the Department of Energy (DOE), Basic Energy Sciences Division and the Laboratory Directed Research and Development at PNNL, which is operated by Battelle for the DOE.

11:20am **SS1-WeM10 Surface Stability of Epitaxial SrRuO@sub 3@ Films***, **A.P. Baddorf**,* Oak Ridge National Laboratory*; J. Shin,* The University of Tennessee*; S.V. Kalinin,* Oak Ridge National Laboratory*; R.G. Moore,* The University of Tennessee*; H.N. Lee, H.M. Christen,* Oak Ridge National Laboratory*; E.W. Plummer,* The University of Tennessee

Strontium ruthenium oxide, SrRuO@sub 3@, may play an important role in oxide electronic devices because of its metallic nature and lattice constant compatible with many transition metal oxide perovskites. Use in device fabrication requires excellent surface and interface stability without reduction or loss of volatile oxides. Thin films of SrRuO@sub 3@ appear to be quite stable, retaining their crystalline nature, as observed with electron diffraction, even after exposure to atmosphere. Surprisingly, this stability disappears after annealing in vacuum to only 200@degree@C. We have studied the surface stability of epitaxial SrRuO@sub 3@ films using a combination of electron spectroscopies, diffraction, and scanning probe microscopy. Epitaxial SrRuO@sub 3@ thin films were grown by pulsed laser deposition using a stoichiometric target on (001) SrTiO@sub 3@ substrates. Atomic force microscopy images taken in air confirm the high quality of the films, showing uniformly spaced terraces with single steps on the film surface, which closely imitate those of the SrTiO@sub 3@ substrate. After reinsertion into vacuum, a (1x1) Low Energy Electron Diffraction (LEED) pattern has been observed at room temperature, revealing an excellent chemical stability in air. The LEED pattern disappears after a brief anneal in vacuum at 200@degree@C, indicating surface disordering. Films were annealed in high vacuum in steps of 100@degree@C up to 800@degree@C and studied after cooling by LEED, x-ray photoelectron spectroscopy, scanning tunneling microscopy and thermal desorption spectroscopy. Loss of SrO from the surface leads to surface pitting and then balling of metallic Ru at temperatures below 400@degree@C. Vibrational spectroscopy relates this monolayer decomposition to submonolayer concentrations of surface hydrocarbons. Stabilities are compared with in-situ films in a new chamber combining high pressure growth with surface characterization.

11:40am **SS1-WeM11 Effect of Polarization on Reactivity of BaTiO@sub 3@ (100)}***, **J. Garra**, B. Halevi, J. Vohs, D.A. Bonnell,* The University of Pennsylvania

Surface reactivity of ferroelectric compounds is an important component of a new approach to nano lithography, may be an interesting catalytic support, and is indicated in ferroelectric memory failure. In order to examine the relationship between atomic polarization and surface adsorption, reactions with single crystal BaTiO@sub 3@ (100) were characterized by temperature programmed desorption, x-ray photo emission spectroscopy, scanning surface potentiometry, and piezo response force microscopy. Similar to the case of other perovskite oxides, water does not adsorb at room temperature or above unless the surface contains a high density of defects. Adsorption of CO2 on BaTiO3 is more complex than on SrTiO@sub 3@. The domain orientation dependence of these reactions will be discussed in the context of proposed reaction mechanisms.

Surface Science
Room 210C - Session SS2-WeM
Semiconductor Surface and Interface Structure

Moderator: A.A. Baski, Virginia Commonwealth University

8:20am **SS2-WeM1 Atomic Structure Determination of @beta@-SiC(001)-(3x2): Experiment and Calculations***, A. Tejeda,* Universidad Autonoma de Madrid, Spain*; D. Dunham,* Northern Illinois Univ.*; F.J. Garcia de Abajo,* CSIC-UPV/EHU and DIPC, Spain*; J.D. Denlinger, E. Rotenberg,* Ernest Orlando Lawrence Berkeley National Lab*; **E.G. Michel**,* Univ. Autonoma de Madrid, Spain*; P. Soukiassian,* Commissariat a l'Energie Atomique and Northern Illinois Univ.

Silicon carbide is a IV-IV compound wide band-gap semiconductor with multiple technological applications. The structure of the Si-rich 3C-SiC(001)-(3x2) surface reconstruction is determined using soft x-ray photoelectron diffraction. Photoelectrons are detected along a full hemispherical sector for different photon energies. The experimental intensity modulations were compared in this work with the results of a suitable scattering formalism that simulates the measured PED by modeling the structure of the last atomic layers. A spherical-wave multiple-scattering cluster formalism was used to reproduce the data and discern the correct surface structure of Si-rich 3C-SiC(001)-(3x2), obtained from a systematic search between the models proposed in the literature. The favored model is a modified version of the two-adlayer asymmetric dimer model (TAADM). An R-factor analysis has been employed to refine this model. We determine the interlayer spacings of the last six atomic layers and find a corrugation of 0.25 Å for the atoms in the outermost dimer. Atoms in the layer underneath dimerize as well, with alternating long and short bond lengths. The long-and-short alternateness between dimer bond lengths explains the top dimmer asymmetry along one single direction. The dimerization takes place through lateral relaxation, without large vertical distortions. The third atomic layer is also dimerized, with a dimer bond length of 2.43 Å. We conclude our results, together with STM and GIXRD experiments, converge in a unifying model for the 3C-SiC(001)-(3x2) surface.

8:40am **SS2-WeM2 Identification of Si and Ge on the Hydrogen-Terminated Ge/Si(001) Surfaces for Observation of Intermixing***, **Y. Fujikawa**, A. Kuwano, M. Kawashima, Y. Yamada-Takamura, T. Nagao, T. Sakurai,* Tohoku University, Japan

Control of the local composition of SiGe films in an atomic level is of great technological importance for designing the SiGe nanodevices. Intermixing effect between Si and Ge is the key issue to achieve precise composition control at the surface layer. It has been known that hydrogen-rich condition at ~300 degree C induces segregation of Si to the surface layer on the Ge covered Si(001) surface, while Ge prefers to stay at the surface layer without hydrogen@footnote 1@. This result implies that the hydrogen-annealing treatment is a useful method to control the composition of SiGe surface layer. We investigated the hydrogen-terminated Ge/Si(001) surface using STM to find that Ge-H sites are imaged as brighter protrusions in comparison with Si-H sites under the empty-state imaging condition. This effect is similar to the case of Cl-terminated Ge/Si(001) surface, which was observed recently@footnote 2@. Si-H and Ge-H sites on the hydrogen-terminated Ge/Si(001) with a Ge coverage of 1.5 ML were resolved successfully using this empty-state imaging condition to study the atomic process of intermixing. Furthermore, it turned out that the Si segregation by the hydrogen-annealing produces significantly bright features beside the dimer-row vacancies (DVLs), in addition to the features coming from Ge-H and Si-H sites. This feature can be attributed to the broken rebonded structure inside the DVL, which contributes the re-adjustment of the surface strain which is modified by the Si segregation. @FootnoteText@ @footnote 1@ Rudkevich et al., Phys. Rev. Lett. 81, 3467 (1998).@footnote 2@ Lin et al., Phys. Rev. Lett. 90, 046102 (2003).

9:00am **SS2-WeM3 The Surface of Silicon-on-Insulator: Structure, Stress, and Three-Dimensional Nanocrystals***, **M. Lagally**,* University of Wisconsin-Madison **INVITED**

Future generations of silicon devices will require approaches beyond the conventional in terms of both fabrication and characterization. In particular, instead of bulk Si, most devices will use silicon-on-insulator (SOI) or variants, such as strained-Si-on-insulator (sSOI), SiGe-on-insulator (SGOI), Si-on sapphire (SOS), and so forth, where in all cases a very thin crystalline layer of Si or SiGe is bound to an oxide or other insulator. Whereas the potential technological value of these materials is without question, what roles do the vacuum-Si and oxide-Si interfaces play? Is there anything interesting that has not already been discovered in the many years in which Si surfaces have been studied? We describe some interesting behaviors. Most important is the presence of strain and the essential instability of the very thin crystalline layer (called the template layer) resting on an oxide. Under appropriate conditions the template layer can dewet, agglomerate, and self-organize into an array of Si nanocrystals. Using LEEM, we observe this process and, with the help of first-principles total-energy calculations, we provide a quantitative understanding of this pattern formation and show how addition of Ge affects the energies and hence the pattern. We have been able to image the surface of SOI with STM, providing insights into the surface structure. Growth of heteroepitaxial films on SOI brings with it unique defect generation mechanisms that are associated with the Si-oxide interface, and a bending of the template that is counterintuitive. We fabricate thin membranes and free-standing structures to investigate the effect of added uniaxial stress on adatom diffusion and the nucleation and coarsening of 2D and 3D structures on this surface. Aspects of the work are supported by NSF, DARPA, ONR, and DOE.

9:40am **SS2-WeM5 Si Epitaxial Growth on Br-Si(100): How Steric Repulsive Interactions Dictate Overlayer Development***, **G.J. Xu**[1], J.H. Weaver,* University of Illinois at Urbana-Champaign

Scanning tunneling microscopy results show the consequences of Si adatom deposition onto Br-saturated Si(100)-(2x1). Those adatoms undergo an exchange reaction with Br but they are immobile at room temperature. In the low coverage regime, annealing to 650 K leads to dimerization, limited ordering, and the formation of short Si chains. Adatom capture by those chains produces features of even and odd numbers of atoms. Annealing at 700 K eliminates the odd chains, but diffusion is highly constrained by Br site blocking. With increased Si coverage, there is further nucleation of chains and chain growth. The local patterning of the Si chains reveals the influence of the strong steric repulsive interactions of Br as out-of-phase structures were favored over in-phase structures around any given chain. Eventually, those interactions favor adlayer (3x2) patches rather than (2x1) islands. Second layer chains appear after the deposition of ~0.3 ML, with layer-2 nucleation at antiphase domain boundaries of layer-1. Bromine loss was observed, even at 650 K, and it is probably tied to the dynamics of atom exchange involved with Si diffusion on a saturated surface.

10:00am **SS2-WeM6 Vacancy Induced Nano-Wire Structure of Ga@sub 2@Se@sub 3@ on Si(100)***, **T. Ohta**, D.A. Schmidt, C.Y. Lu, Q. Yu, M.A. Olmstead, F.S. Ohuchi,* University of Washington

We report formation of nano-wire structure of gallium-selenide (Ga@sub 2@Se@sub 3@) grown on arsenic terminated silicon (Si) (100). Ga@sub 2@Se@sub 3@ crystallizes into a defected zinc-blende structure with every third of the Ga site vacant. Vacancies are necessary to maintain charge neutrality in the crystal, and are responsible for its highly anisotropic electrical and optical properties by ordering into line geometry. Scanning tunneling microscopy (STM) revealed that wire structure is two-unit-cell-wide with the separation between wires of about three-unit cell, and its direction is influenced by alternating symmetry of the initial substrate. We will discuss its atomic structure, evolution of its initial growth and the interface structure between Ga@sub 2@Se@sub 3@ and Si, based on our recent investigation using STM and core-level photoemission spectroscopy (PES). It is shown that the formation of the wire structure is strongly related to the ordering of structural vacancies, and we will present its growth model. This formation mechanism is unique to the prevalence of structural vacancies incorporated in Ga@sub 2@Se@sub 3@, unlike other nano-structure formation mechanisms driven by defects or strain, such as for InAs nanodots on GaAs or SiGe clusters on Si. This work is supported by NSF Grant DMR 0102427 and M. J. Murdock Charitable Trust. T. O. further acknowledges support from University Initiative Fund of the University of Washington, and D. A. S., UW-PNNL Joint Institute for Nanoscience research award.

10:20am **SS2-WeM7 STM Study of Silicon Surfaces at P-N Junctions Prepared by Low-Temperature Processing***, **T.-C. Shen**,* Utah State University*; J.S. Kline, J.R. Tucker,* University of Illinois at Urbana-Champaign

Dopant distribution at p-n junctions has been extensively studied by many techniques. Recent advance of electron devices further demands a thorough understanding and precise control of the dopant behavior at nanometer scale. Feenstra et al. pioneered the technique of cross-sectional STM to image the p- and n-type GaAs interface. To examine planar p-n junctions in Si, conventional high temperature surface preparation in ultrahigh vacuum is not suitable due to enhanced dopant diffusion and desorption. In this presentation, we report some of our experimental findings based on a previously developed low-temperature surface preparation technique involving 300eV Ar ion sputtering and 600-700°C annealing. The B-doped substrates used in this work are either at an impurity level of 3x10@super 17@ cm@super -3@ or 1x10@super 19@cm@super -3@. N-type patterns are fabricated by implanting 40-50 keV As ions at a dose of 1x10@super 15@cm@super -2@ into the B-doped substrates. The atomically clean and flat surfaces prepared at low temperatures allow us to obtain atom-resolving images both in the As-implanted region and the B-doped substrate as well as their original interface. We observe for the first time that heavily B-doped substrates lead to c(4x4) patterns on the surface the same as the result of diborane exposure. When terminating the surface with H, we find that the dangling bonds in the As-region are much brighter than those on the substrate. More c(4x4) regions and less C and H-induced clustering are observed in the As region. Surface topography at different annealing conditions, the role of dopant atoms in the diffusion of other impurities and their electronic effect will be discussed. This work is supported by DARPA-QuIST program under ARO contract DAAD 19-01-1-0324.

10:40am **SS2-WeM8 Hydrogen Interaction with a Si(113)-3x2 Surface***, **M. Yoshimura**, K. Mamiya, K. Ueda,* Toyota Technological Institute, Japan

Since the Si(113) surface is thermally stable and has a low energy compared to that of the low-index surfaces such as Si(111) and Si(001), it is expected to a good substrate for epitaxy in semiconductor technology. The clean surface reconstructs into a 3 x 2 superstructure consisting of pentamers and adatoms, as was proposed by Dabrowski et al.@footnote 1@ Each 3 x 2 cells contain a subsurface interstitial located below one of the tetramers, which lowers the total surface energy. On the other hand, hydrogen termination is one of important techniques in the silicon-based device processes. However, hydrogen interaction with the Si(113) has been studied only by spectroscopic measurements such as electron energy loss spectroscopy (EELS)@footnote 2@. Here, we report ultrahigh vacuum scanning tunneling microscopy (UHV-STM) study of the atomic hydrogen adsorption onto the clean Si(113)-3 x 2 surface on an atomic scale. A Si(113) surface was cleaned by a conventional procedure and was exposed at room temperature to atomic hydrogen by cracking of hydrogen molecules using a hot tungsten filament. After 10 L exposure, the reduction in the density of states around Fermi level was confirmed by scanning tunneling spectroscopy (STS). STM images revealed clearly that some adatoms were missing and some pentamers changed their image contrast, probably due to hydrogen adsorption at the surface dangling bonds of the corresponding sites. The clustering was not observed up to this exposure level. Based on the results of STM/STS together with low-energy electron diffraction (LEED), we discuss the initial adsorption processes of atomic hydrogen on Si(113)-3x2 at an atomistic level. @FootnoteText@ @footnote 1@ J. Dabrowski et al., Phys. Rev. Lett. 73 (1994) 1660.@footnote 2@ K. Jacobi and U. Meyer, Surf. Sci. 284 (1993) 223.

11:00am **SS2-WeM9 Application of the Simplified Bond-Hyperpolarizability Model to Bulk Second- and Third-Harmonic Generation in Semiconductors***, **H.J. Peng**, E.J. Adles, D.E. Aspnes,* North Carolina State University

Application of nonlinear optical (NLO) spectroscopies to the analysis of surfaces and buried interfaces of crystalline semiconductors requires an understanding of the contributions from the second- and third-harmonic generation (SHG, THG) from the bulk. THG is particularly relevant because for reasons of macroscopic symmetry THG is the lowest NLO effect that can be used to study the surfaces and interfaces of (001)Si, which underlies integrated-circuits technology. We show that the simplified bond-hyperpolarizability (SBHM) model that we previously developed to analyze surface and interface contributions to second- and fourth-harmonic generation data for Si provides an accurate description of bulk THG of Si with no adjustable parameters beyond amplitude scaling. The SHG contribution, which is nominally forbidden in Si, can be evaluated from the known linear-optic response and, contrary to some speculation, is found to be negligible for this material. These results are expected to be applicable to other semiconductors as well, thereby simplifying the analysis of surfaces and interfaces by NLO techniques.

11:20am **SS2-WeM10 Second Harmonic Generation from Metallic Quantum Wells on Si(111) Surfaces***, **K. Pedersen**, T.G. Pedersen,* Aalborg University, Denmark*; P. Morgen,* SDU Odense University, Denmark

Optical second harmonic generation (SHG) from materials with bulk centrosymmetry such as metals and a number of elemental

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

semiconductors is surface and interface sensitive due to the lack of electric dipole contributions to second-order nonlinearities in the bulk of such materials. Thin films on a substrate, having two dissimilar boundaries, are thus expected to be interesting objects for SHG studies. The buried interface can be reached even through 50 to 100 layers of metal but the interface signal appears coherently added to contributions from the free surface. Resonant electronic transitions that may appear in SHG spectroscopy can thus be localized either at the free surface or at the buried interface. Under proper growth conditions thin metallic films on semiconductors form crystalline layers showing sharp quantum well (QW) levels in photoemission spectroscopy. In SHG the discrete QW levels result in oscillating signals as the system passes through a series of resonant transitions between occupied and empty states for growing film thickness. In the present work electronic transitions at the buried interface are identified through the dispersion of quantum well resonances seen with SHG. Recordings of SHG from a wedge shaped Ag film (0-50 layers) grown on Si(111)7x7 surface show that resonances disperse toward lover thickness for growing photon energy. Shifts or breaks in dispersion curves appear when the phase of the interface signal changes at resonant electronic transitions. In addition to expected transitions near critical points of bulk Si an interface resonance is found between the two lowest critical points of bulk Si.

11:40am **SS2-WeM11 Spectroscopic Second Harmonic Generation on Hydrogenated Amorphous Silicon Surfaces and Interfaces***, **C.M. Leewis**, J.J.H. Gielis, I.M.P. Aarts, M.C.M. van de Sanden, W.M.M. Kessels,* Eindhoven University of Technology, The Netherlands

Optical Second Harmonic Generation (SHG) is applied on hydrogenated amorphous silicon (a-Si:H) films on fused silica substrates to investigate the presence of surface and buried interface dangling bonds. For amorphous material, e.g. a-Si:H, the SHG technique is surface-specific and therefore originates from both the film surface and the film-substrate interface. The origin of the second harmonic signal can be due to dangling bonds and strained bonds. In addition, optical interference effects can enhance the signal for certain wavelength-film thickness combinations. The technique is applied both ex situ, and in situ in a UHV setup on hot wire grown films. An incident polarization scan is performed for both p- and s-polarized SHG radiation while SHG is also measured while rotating the sample around the axis normal to the substrate. It has been established that the SHG can be described by the infinity-m symmetry class, which is in agreement with the amorphous nature of the material. In situ spectroscopic scans are performed with a probe photon energy in the range 1.0-1.6 eV for different polarizations. These scans are in agreement with ex situ scans on plasma deposited a-Si:H. The observed resonant peaks correspond possibly to surface and interface dangling bond states@footnote 1@. The presence of dangling bonds is investigated with real time measurements. These experiments during film growth have already shown that the SHG intensity increases instantly when growth is started, and gradually decreases during further growth. In addition, it is shown that the maximum SHG intensity increases for increasing substrate deposition temperatures in the range 520-720 K. The consequences for a possible surface and interface concentration of dangling bonds will be discussed. @FootnoteText@ @footnote 1@Pedersen et al., Phys. Rev. B 52, R2277 (1995).

Thin Films
Room 303C - Session TF-WeM
Optical Thin Films

Moderator: G. Ockenfuss, OCLI - JDS Uniphase

8:20am **TF-WeM1 Optical Properties of Uranium and Thorium-Based Thin Films as Highly Reflective EUV Mirrors***, D.D. Allred, J.E. Johnson, **W.R. Evans**, N. Farnsworth, A.E. Baker, R.S. Turley,* Brigham Young University

We present measured reflectances (Beamline 6.3.2, ALS at LBNL) of air oxidized sputtered uranium and thorium, reactively sputtered (O2) uranium oxide and thorium, and reactively sputtered (N2) uranium nitride thin films. The thin films were also characterized using AFM, spectroscopic ellipsometry, LAXRD, TEM, XPS, and XANES. We compare these with our measurements of the reflectance of nickel, gold, and iridium thin films (commonly used soft x-ray reflectors for astronomy and synchrotrons) from 50 to 500 eV at 5Ës, 10Ës, and 15Ës grazing incidence. These show that these two uranium compounds, as UO2 and UN, and thorium as air oxidized thorium can fulfill their promise as the highest-known, single-surface reflector for this portion of the soft x-ray region, being nearly twice as reflective as nickel in the 120 to 200 eV region. We additionally report complex indices of refraction for ThO2, UO2, and UN obtained from reflection and transmission measurements taken at the ALS. Shifts in energy of up to 20 eV between features in the Th spectra suggest the need for possible revision in the atomic scattering factor approach for obtaining optical constants for compounds. There are also important discrepancies between UO2â?Ts and UNâ?Ts actual reflectance with those estimated using the atomic scattering factor approach.

8:40am **TF-WeM2 Determining Physical and Chemical Properties of Sputtered Uranium and Thorium Thin Films Useful as Extreme Ultraviolet Reflectors***, **R.W.L. Larsen**,* Provo High School*; D.D. Allred,* Brigham Young University

As applications for extreme ultraviolet radiation have been identified, the demand for better optics has also increased. Recently, sputtered thin films containing uranium and thorium have been shown to produce the highest low-angle reflectors for portions of the EUV/soft x rays. For more progress to be made in this area optical constants needed to be obtained. In addition, optical properties need to be assigned to specific compounds and structures. The purpose of this project was to determine the composition, density, lattice structure, and roughness of these sputtered uranium and thorium thin films and their oxides and nitrides via TEM, XPS, AFM and to relate these structural effects to the reflectance of the thin films. We have found that the thorium samples oxidize more slowly in air than uranium so we can talk about the reflection of these films being a mixture of thorium and thorium oxide. Sputtered uranium on the other hand quickly becomes uranium dioxide which is moderately stable for periods of months. Whereas the sputtered uranium nitride samples are uranium mononitride only in the bulk and their surfaces become oxidized.

9:00am **TF-WeM3 Mechanical Characteristics of Optical Films: Their Origin and Evaluation***, **L. Martinu**, J.E. Klemberg-Sapieha,* Ecole Polytechnique Montreal, Canada **INVITED**

Control of the mechanical properties is essential in order to achieve reliable performance of optical thin film systems such as filters, waveguides, optical MEMS, sensors, optical coatings on plastic substrates and others. Mechanical properties are closely related to the film microstructure and composition that, in turn, depend on the choice of materials and processes and on the energetic conditions during deposition. In order to assure successful performance and high stability of optical films, the mechanical properties have to be optimized together with the optical characteristics and other film functional properties (electrical conductivity, thermal and environmental stability, surface energy etc.). This presentation will give an overview of the methodology of mechanical testing and will describe the advantages and limitations of individual methods. We will concentrate on the effect of process parameters on the mechanical properties of the individual low, medium and high index optical films, especially those prepared by Physical Vapor Deposition (PVD) and Plasma Enhanced Chemical Vapor Deposition (PECVD). After a detailed review of the basic mechanical properties of films and substrates used in optical applications, we will illustrate the advances in this filed by examples of complex optical systems in which the control of the mechanical behavior is particularly important. This includes a comparison between inhomogeneous and multilayer films, optical coatings on plastics, complex optical filters used in optics, optoelectronics, photonics, architecture, and in medical, security, aerospace, automobile and other applications.

9:40am **TF-WeM5 Improved Optical Heterodyne Detected Transient Grating Method by using a Thin Film Grating***, **K. Okamoto**, Z. Zhang,* California Institute of Technology*; D.T. Wei,* Wei & Assoc.*; A. Scherer,* California Institute of Technology

Transient grating (TG) spectroscopy based on the third order nonlinear optical effect has been applied to material, chemical, and biological research. Optical heterodyne detected (OHD) TG measurements have been reported by several groups, but experimental setups were mostly complicated. Here, we demonstrate a convenient new technique of OHDTG by transferring a pattern directly from a metal film grating into sample solution. This method has the same advantages of existing OHDTG techniques but the setting is much simpler. Thin film gratings having submicron periods are fabricated by: evaporating metal on a glass substrate, laser beam writing lithography, and chemical etching. The narrowest metal width of our grating is 333nm. The fabricated grating is then placed in the front side of a quartz cell containing the sample solution with 10mm optical pass length. An UV pump beam (a frequency-tripled Nd:YAG laser) casts a shadow from the grating to the sample solution such that a dark/bright pattern is formed in the solution liquid called transient grating. Such spatial modulation of the optical intensity induces changes of temperature, density and the molecular excitation. Through this transient grating, the modulated refractive index and absorbance of sample materials can be detected by the diffraction of a probe beam (a He-Ne laser). By analyzing the probe beam diffraction, we can obtain the intensity and dynamics of the modulated parameters named above. This technique has many advantages compared with existing OHDTG techniques; such as: (1) simple setting, easy alignment, (2) high signal stability, (3) easy control of phase shift, and (4) quick interchange of grating periods. We shall demonstrate this technique from several materials and discuss about the potential benefit of this new technique.

10:00am **TF-WeM6 Infrared Emission from Zinc Sulfide Doped with Rare Earth Fluorides***, **D. DeVito**, A. Kale, W. Glass, M. Davidson, P.H. Holloway,* University of Florida

Thin film electroluminescent devices are excellent sources for high efficiency infrared emission. Rare earth elements, such as Erbium, Thulium and Dysprosium, are good dopants for infrared emitting phosphors because of the many transitions they exhibit in the infrared region. Zinc sulfide is a stable, wide bandgap semiconductor in which electrons can be excited to appropriate energies to produce excitation of the luminescent centers. Achieving good brightness requires a combination of precise composition, deposition conditions and post-deposition annealing. Lanthanide doped zinc sulfide electroluminescent thin films were deposited from two planar magnetron sources using ZnS and lanthanide trifluoride targets. Infrared emission from devices shows a marked improvement for films annealed at temperatures above 350°C. Maximum brightness was achieved for samples annealed at 425°C and, based on SIMS data, is associated with a reduction in the fluorine concentration in the films. Mechanisms for the loss of fluorine include solid state diffusion, with replacement of F with S on the substitutional site. The mechanism for increased electroluminescence will be discussed based on oscillator transition strength relative to nearest neighbor bonding.

10:20am **TF-WeM7 Spectrally Stable Optical Coatings Using Closed Field Reactive Magnetron Sputtering***, **J.M. Walls**, D.G. Gibson,* Applied Multilayers Ltd, UK

Magnetron Sputtering has many advantages for the deposition of multilayer optical coatings. The sputtering process is "cold", making it suitable for use on the widest range of substrates including polymers. This paper will describe the "Closed Field" process that allows high quality, multilayer metal-oxide thin films to be deposited at high rates with exceptionally low absorption. In contrast to previous reactive dc sputtering strategies the Closed Field process does not require a separate ion or plasma source. The Closed Field creates a magnetic bottle that extends the electron mean free path leading to high ion current densities. The combination of high current densities with ion energies in the range 30eV to 50eV creates optimum thin film growth conditions. As a result the films are dense and spectrally stable. Also, they are exceptionally smooth as measured using FEGSEM and Coherence Correlation Interferometry Examples of the morphology and optical properties of single layer electrically insulating (SiO2, Nb2O5 and TiO2) and conducting meat oxides (ITO) will be presented. The structure and morphology of a series of multi-layer metal oxide coatings will also be presented These will include ant-reflective coatings, UV and infra-red blockers, lighting filters and conductive oxides for flat screen displays.

10:40am **TF-WeM8 Multilayered SiN@sub x@/SiO@sub 2@ AR Coatings with Cylindrical Cathode by Unbalanced Compressive Magnetron Sputtering***, **C.-S. Wang**, K. Sasaki,* Kanazawa University, Japan*; S.-F. Chen,* National Taipei University of Technology, Taiwan*; T. Hata,* Center of Optical Coating Research, Japan

Excellent adhesion and high throughput production of anti-reflection (AR) coatings were examined by high and low refraction index SiN@sub x@/SiO@sub 2@ combined system. In general, the refraction of SiN@sub x@ was strongly dependent on the composition of nitrogen and it is difficult to obtain stoichiometric SiN@sub x@ in state-of-the-art techniques. In order to satisfy the requirements, we employed a cylindrical unbalanced compressive magnetron (UCM) sputtering technique. A pair of permanent magnets was adjacent to a cylindrical rotating target to increase and compress the ionization density in the region near the substrates. And the reactive gases were introduced between the cathode and UCM so as to produce discharge uniformly. We used a plasma-sprayed Si cylindrical target (6 cm in diameter and 50 cm in length) in which a 4.5 kGauss permanent magnet was built-in. Moreover, the same magnets were also sited to the both sides of the target to form convergence plasma stream forward to a glass substrate. The distance of target to substrate was 5 cm. SiN@sub x@ and SiO@sub 2@ films were deposited by alternatively changing N@sub 2@ and O@sub 2@ gases. The deposition rates of the films were as large as 2.01nm/s and 2.23nm/s respectively. The refraction index of SiN@sub x@ films was varied from 1.63 to 1.75 at 500 nm wavelength by varying Ar/N@sub 2@ flow ratio from 1 to 0, while that of SiO@sub 2@ films was 1.45 stably. According to AR simulation using above values, 4 layers system of SiN@sub x@/SiO@sub 2@ satisfies a reflection less than 1% in wide visible range (420~680 nm). Whole process without evacuation was completed within just 4 min. Additionally, according to spectroscopic ellipsometory measurement, the extinction coefficient was small resulted that high density and less defective films were obtained. This technique is useful for large scale and high performance AR coatings.

11:00am **TF-WeM9 Analysis of a Combined Sputtering and Plasma-Heating-Evaporation Process of Magnesium Fluoride by using Plasma Emission Spectroscopy and Energy Resolved Type Mass Spectrometry***, **T. Deguchi**,* Kanazawa Institute of Technology, Japan, Ishikawa*; T. Sasaki, E. Kusano,* Kanazawa Institute of Technology, Japan*; S. Iura, K. Kawamata,* Olympus Co., Ltd., Japan*; A. Kinbara,* Kanazawa Institute of Technology, Japan

A sputtering deposition process combined with plasma-heating-evaporation is an attractive technique to deposit MaF@sub 2@ thin films onto unheated substrate. However, poor understandings of the mechanisms prevent stabilization of the process. In this study, we have analyzed the process by using plasma emission spectroscopy and energy resolved type mass spectrometry. A sputtering machine used for mass spectrometry was a UHV system equipped with a 55 mm diameter cathode and that for film deposition and plasma emission spectroscopy was a commercial batch type system equipped with a 75 mm diameter cathode. The plasma process monitor (PPM-421, Balzers AG) was used to analyze a mass/charge ratio and energy of ions arriving to the substrate. A spectrometer (TYPE HR-2000, Ocean Optics) was used for plasma emission spectroscopy. Ions typically detected were Mg@super +@, F@super +@, MgF@super +@ both in Ar and O@sub 2@ atmospheres. While in Ar atmosphere the number of MgF@super +@ decreased with increasing rf plasma power, in O@sub 2@ atmosphere it increased drastically after the plasma power exceeded 250W. At this point in O@sub 2@ atmosphere the plasma-heating-evaporation occurred. Results obtained by the plasma emission spectroscopy well agreed to these results; i.e., the emission intensity ratio MgF@super *@/O@super *@ increased significantly at an rf power of 200W. Furthermore, the high energy tail in ion energy spectra, resulting from momentum transfer in sputtering process, observed for Mg@super +@ or F@super +@ in Ar atmosphere disappeared for those in O@SUB 2@ atmosphere, showing that the evaporation process in O@sub 2@ atmosphere was not dominated by sputtering, but by thermal evaporation.

11:20am **TF-WeM10 Silicon-rich Nitride Characterization for Polysilicon Gate Patterning***, **F. Celii**, K. Hewes, S. Zheng, E. Mickler,* Texas Instruments

For manufacturable patterning of sub-0.10 µm poly-Si gates, advanced etch techniques must complement current lithography capability. One approach uses photoresist line-narrowing combined with an etch hardmask that serves the dual purpose of forming a low-reflectivity patterning substrate. The hardmask suitability is determined by the poly-Si etch resistance, the optical properties (if used as an anti-reflection coating (ARC) layer) and integration issues (e.g., cleanup and cost). The requirements on the hardmask will change with subsequent generations, as the material stack layers and thicknesses change. We report the characterization of silicon-rich nitride (SRN) films used in poly-Si gate patterning. SRN films were deposited by PECVD in commercial reactors. Initial characterization used variable-angle spectroscopic ellipsometry (VASE), over the wavelength range 140 - 1100 nm. Modeling of the VASE data provides optical constants at lithography wavelengths (193, 248 nm) of the various film compositions. Based on previous work, the spectral dependence of the optical constants also provided a measure of the Si-loading of the film. The Si-content of the previously-studied sample set (37 to 41%),@super 3@ which gave k@sub 193@ values up to 1.0, was significantly extended with the current set, with k@sub 193@ values up to 2.0. Moreover, the (n,k) values of the current SRN films fall along a fairly narrow line. Additional characterization of these films will include composition measurement by RBS spectroscopy and FT-IR spectroscopy characterization over 400 - 4000 cm,@super -1@ which yield an independent measure of Si-dimer concentration. Simulations of gate patterning structures show (n,k) values which yield reasonable patterning process margin. CD swing curves of patterned films will also be presented.

11:40am **TF-WeM11 Film Stress and Discharge Properties of MgO protective layer of AC-PDP*, M.J. Lee,* *S.Y. Park, S.H. Moon, S.G. Kim,* Seoul National University, Korea*; H.J. Kim,* Seoul National University, Korea, South Korea

To increase the lifetime of PDP (Plasma Display Panel), MgO thin films are applied on dielectric layer to protect the dielectric layer from ion bombardments of plasma. Because MgO film is unlikely sputtered by ion bombardments and reduces the discharge voltage of PDP due to high secondary electron emission coefficient (@gamma@@sub i@), in turn less energy consumption. In this work, discharge characters of PDPs related to the stress formed in MgO thin films are investigated. MgO thin films were deposited on glass substrate with dielectric by e-beam evaporation in vacuum chamber, 5 x 10 @super -7@ Torr. Substrate temperature was varied from room temperature to 300°C, then annealing process is carried out at 300°C in vacuum chamber for 1hr and 3 hr respectively. The stresses of each sample were measured by laser scanning method to detect the substrate curvature change. To examine the effect of the change of stresses in MgO layers in different formation process on discharge character of real panel, firing voltage (V@sub f@) and sustaining voltage (V@sub s@) were observed. Surface roughness, morphology, and crystallographic preferred orientation of MgO films were also evaluated by XRD, AFM, SEM. And the impurities and hydrates of MgO surface before and after annealing were analyzed by XPS. MgO films on glass substrate have compressive stresses, which were varied according to deposition condition. After the annealing, the compressive stresses were released relatively, and definitely changed at specific temperature condition. The relation between the discharge characters and MgO thin film stress change and the relevancy with other properties of films was also evaluated.

Vacuum Technology
Room 303D - Session VT-WeM

Contamination Control, Outgassing and Modeling

Moderator: T. Gessert, National Renewable Energy Laboratory

8:20am **VT-WeM1 Ultra Cleaning Techniques and Their Use in Vacuum Technology*, P.H. LaMarche,*** Princeton University **INVITED**

A number of conditions have come together over the last ten years that have significantly advanced the state of the art in cleaning technology. The semiconductor industry has reduced feature size to the sub-100-nanometer scale, ultra-low particle counting techniques have pushed the boundaries of cleanliness for low backgrounds, and emissions regulations have become very stringent. These and other circumstances have conspired to drive substantial changes in cleaning technology, equipment, and the industries involved. In this talk, we shall examine the changes in cleanliness requirements, the concomitant changes in cleaning technology and how these changes benefit vacuum technology and those technologies that are of importance to the members of the AVS.

9:40am **VT-WeM5 Contamination Control in PECVD Processes*, B. Shin,*** *Y. Uritsky,* Applied Materials*; T. Gessert, J.P. Benner,* National Renewable Energy Laboratory*; R. Childers, H.S. Ryu,* Hynix **INVITED**

The semiconductor industry is presently migrating chip manufacturing toward the sub-100-nm technology node, which is like splitting a strand of hair more than 1,000 times. Typically, more than 350 process steps are involved in fabricating these wafers, including depositions of oxides and nitrides by plasma-enhanced (PE) CVD, plasma etching steps, and final passivation. In this paper, we will examine the industry requirements on contamination control while optimizing process capability, throughput, and overall production efficiencies. The paper will also discuss how process integration and production automation are enabled by technologies involving in-situ cleaning and in-situ particle monitoring incorporated into the production tools, achieving enhanced process stability and production efficiency.

10:40am **VT-WeM8 Pressure Compensation for a Radiation-Induced Current Caused in a Vacuum Gauge Cable in the SPring-8 Storage Ring*, T. Magome,*** *H. Saeki,* Japan Synchrotron Radiation Research Institute, Japan

Several hot-cathode-ionization gauges (B-A gauges) located near photon absorbers, have been under a radiation environment with a dose rate less than 1.8x10@super 2@Gy@sub air@/Ahr in the SPring-8 storage ring. A pressure-measurement error caused by a radiation-induced current in a collector cable, has been observed as a low-pressure indication in this environment. To find an actual pressure, such a pressure-measurement error in the collector cable was compensated using a radiation-induced current measured with a reference cable. As the result, the compensated pressure showed the actual pressure with a ±24% error in the pressure range from 10@super -9@Pa to 10@super -8@Pa in a stored-electron-beam condition. Furthermore a new cancellation method using a single signal cable will be tested in near future.

11:00am **VT-WeM9 Development of Horizontal NEG Coating Cathode for Long Accelerator Beam Tubes*, D. Weiss,*** *H.C. Hseuh, R. Todd, P. He,* Brookhaven National Laboratory

The Relativistic Heavy Ion Collider (RHIC) at Brookhaven National Laboratory (BNL) is a superconducting heavy ion collider with two rings of 3.8 km circumference for high energy and nuclear physics research. As ion beam intensity increases so do pressure rises at RHIC room temperature ultrahigh vacuum (UHV) regions that limit further intensity gains. The pressure rises are associated with electron multi-pacting, electron stimulated desorption and ion desorption. NEG coated beam pipes have been proven effective to combat pressure rises in synchrotron radiation facilities and will be added to a significant portion of the UHV room temperature regions of RHIC. Standard stainless steel RHIC beam pipes have been NEG coated by vendors. Some special beam pipe assemblies in the RHIC experimental regions are made of beryllium and will be NEG coated at BNL. A NEG coating cathode, similar to the cathode in the low cost high yield cylindrical magnetron sputtering system developed by BNL for titanium nitride coating, has been developed to coat these special beam pipes. This cathode can accommodate chambers with lengths up to 4 meters. This system features a hollow, liquid cooled cathode that can achieve continuous sputter rates of several amps per meter. The stiffness and support of the cathode allows chambers to be coated in a horizontal position. The cathode comprises a hollow titanium tube partially covered with zirconium and vanadium ribbons. The ribbons are arranged to provide a uniform sputtering distribution and results in an acceptable NEG mixture deposited on the substrate. Vacuum performance of the NEG coated pipes was measured and coating properties analyzed with auger electron spectroscopy and scanning electron microscopy. The system design, development, and analysis results are presented.

11:40am **VT-WeM11 Slip Fluid Model of a Holweck Vacuum Pump in the Viscous and Transition Regime*, S. Giors,*** Varian S.p.A., Italy*; F. Subba, R. Zanino,* Dipartimento di Energetica, Italy

Computational Fluid Dynamics (CFD) is playing an increasingly important role in the study of rarefied internal flows in vacuum pumps. Holweck pumps are used as high pressure stages in modern hybrid turbomolecular vacuum pumps, to extend the maximum compression ratio up to outlet pressures in the 1-10 mbar range, corresponding to the transition and the viscous laminar regime, for the typical pump's dimensions. The study of Holweck pump stages in the viscous regime has been carried out by Boulon et. al.@footnote 1@, using a no-slip fluid model. They show a good level of agreement with experimental data, but the accuracy of their model decreased for pressures corresponding to Knudsen number Kn>0.01. They suggest the need of slip boundary conditions to improve the accuracy of the model. In this work a three-dimensional model for the Holweck pump, based on the Navier-Stokes equations, with viscous slip and thermal jump boundary conditions is developed and a commercial CFD code is used to solve it in an outlet pressure range corresponding to the viscous laminar regime and transition to molecular flow for an experimental pump. The validation against the experimental data shows a good level of accuracy in terms of both compression ratio and dissipated mechanical power, up to Knudsen number Kn=0.1. @FootnoteText@ @footnote 1@ O. Boulon, R. Mathes, "Flow modeling of a Holweck pump stage in the viscous regime", Vacuum 60, 73-83 (2001).

Science of Semiconductor White Light Topical Conference
Room 304B - Session WL-WeM

Science of Semiconductor White Light I

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

8:20am **WL-WeM1 Solid State Lighting*, M.R. Krames,*** Lumileds Lighting **INVITED**

Rapid progress in organometallic vapor phase epitaxy of III-phosphide and III-nitride compounds in the 1990's paved the way for the development of advanced visible-spectrum light emitting structures based on AlGaInP and InGaN active layers, respectively. These material platforms have been introduced into novel, high power, device architectures for dramatic improvements in total light generation and extraction efficiency, resulting in solid state light sources with external quantum efficiencies in the range of 30-50%. In particular, advances in the III-nitride blue and near-ultraviolet devices have enabled the efficient generation of white light through excitation of down-converting phosphors such as YAG:Ce. High power white LEDs are now commercially available with luminous efficiencies of 30-40 lm/W, exceeding that of standard incandescent (~17 lm/W) and halogen (~25 lm/W) bulbs. In addition, new classes of phosphors are being developed to further improve the emission spectral content, and thus color rendering quality, of white LEDs towards applications in indoor and retail illumination. The current state of the art for such solid state light sources will be reviewed, along with an outlook towards future applications and performance.

9:00am **WL-WeM3 Growth of AlGaN-based UV LEDs Emitting at ~280 nm by Metalorganic Chemical Vapor Deposition***, **R.D. Dupuis**, U. Chowdhury, P. Li, J.-H. Ryou, T. Chung, D. Yoo, J.-B. Limb,* Georgia Institute of Technology **INVITED**

Wide-bandgap nitride semiconductor materials in the InAlGaN system have attracted attention for deep-ultraviolet (UV) optoelectronic device applications in the spectral range lambda<300nm. In this paper, we report on the status of ternary AlGaN-based UV-LEDs emitting at ~280 nm. These devices are fabricated from epitaxial layers grown using the low-pressure metalorganic chemical vapor deposition (LP-MOCVD) technology. The epitaxial layers are grown on dual-side polished c-plane sapphire substrates and the structure is designed for "flip-chip" operations where light is extracted from the back-side of the substrate. The device structures typically consist of an AlN buffer layer and a low-resistivity n-type Al@sub 0.6@Ga@sub 0.4@N:Si window layer in order improve light extraction while maintaining a low device series resistance and a low spreading resistance. A typical active region consists of three 10nm Al@sub 0.48@Ga@sub 0.52@N:Si barriers with three 5nm Al@sub 0.40@Ga@sub 0.60@N:Si quantum wells. The p-side cladding layer structures generally consist of a 20nm p-type Al@sub 0.52@Ga@sub 0.48@N:Mg electron barrier and a 20nm Al@sub 0.40@Ga@sub 0.60@N:Mg p-type cladding layer (or an AlGaN superlattice cladding layer) while a 25nm GaN:Mg is employed as a p-contact cap layer. We also report on the use of InGaN:Mg p-type layers to reduce the resistance of the p-contact layer in UV LED structures. Due to the lower acceptor ionization energy and lower work function, InGaN:Mg promises or offer better p-layer current spreading and lower contact resistance compared to GaN:Mg. The results of a study of the growth of InGaN:Mg along with Ohmic contact characteristics is described for application to UV-LED structures. The performance of UV LEDs fabricated from these materials will be described.

10:20am **WL-WeM7 Surface Chemistry and Film Growth during ZnO Atomic Layer Deposition***, **S.M. George**,* University of Colorado **INVITED**

Atomic layer deposition (ALD) is a thin film growth technique based on sequential, self-limiting surface reactions. ZnO ALD can be achieved using sequential exposures of Zn(CH@sub2@CH@sub3@)@sub2@ [diethylzinc (DEZ)] and H@sub2@O at 180°C. This talk will characterize the surface chemistry and film growth during ZnO ALD using in situ quartz crystal microbalance (QCM), Fourier transform infrared (FTIR) spectroscopy and 4-point probe resistivity measurements. The QCM measurements display a staircase structure that is consistent with a mass increase of 110 ng/cm@super2@ or 2.0 Å per DEZ/H@sub2@O reaction cycle. The FTIR results show that the growing ZnO surface displays vibrational modes consistent with ZnOH* species following the H@sub2@O exposures. DEZ exposure converts these species back to Zn(CH@sub2@CH@sub3@)* species. The background infrared absorbance of the ZnO film also increases progressively with number of DEZ/H@sub2@O cycles as expected for an electrical conductor. The 4-point probe investigations reveal dramatic oscillations in the ZnO film resistivity that are dependent on both film thickness and adsorbed surface species. The resistivity is much higher with ZnCH@sub2@CH@sub3@* species than with ZnOH* species. This resistivity dependence on surface species may be important for an understanding of ZnO gas sensors. The ZnO ALD films are polycrystalline and have an electrical resistivity of ~10@super-2@ @ohm@cm. Excellent ultrathin and conformal ZnO ALD films are observed on ZrO@sub2@ and BaTiO@sub3@ particles.

11:00am **WL-WeM9 Efficiency Limitations of Solid-State Sources used in General-Lighting Applications***, **E.F. Schubert**, Y.-L. Li, J. Kim, T. Gessmann,* Rensselaer Polytechnic Institute **INVITED**

The use of highly efficient solid-state light sources for illumination applications can enable huge energy savings, a reduced generation of green-house gases, and a reduction in environmental pollution. Luminous source efficiencies exceeding 300 lm/W and color-rendering indices (CRIs) greater 90 are feasible with solid-state sources. This talk discusses critical issues in solid-state lighting including practical limits to efficacy and efficiency, scalability of chip size, and scalability of current density. Possible solutions to these issues based on new materials and structures are presented including low-refractive index materials, omni-directional reflectors, and polarization-enhanced contacts. Furthermore it is shown that solid-state sources based on light-emitting diodes (LEDs) have advantages not offered by conventional light sources, namely tunability and adaptability. Future smart light sources based on LEDs could offer full tunability of their spectral composition, color temperature, and other parameters, thereby allowing for the optimization of light sources for specific applications. Several application areas and the potential benefits of smart light sources are discussed.

Wednesday Lunch, November 17, 2004

Exhibitor Workshop
Room Exhibit Hall B - Session EW-WeL

Advances in SPM and Other Analytical Techniques

Moderator: M. Lagally, University of Wisconsin-Madison

12:00pm **EW-WeL1 Quantitative and Chemical State Analysis of Cross-Sectional GaAs/AlAs Superlattice Using the Newly Developed Scanning Auger Nanoprobe***, **M. Suzuki**, N. Urushihara, N. Sanada, A. Yamamoto, H. Iwai, R. Oiwa, Y. Ohashi,* ULVAC-PHI, Inc., Japan

Using Auger electron microscopy, so far, because of the electron beam diameter, thermal/mechanical drift and noise, it has been difficult to achieve a spatial resolution of less than 10 nm. The newly developed scanning Auger nanoprobe (PHI-700) consists of a cylindrical mirror analyzer with a coaxial Schottky field emission electron gun and an eight channel multi-channel detector. The instrument is housed in an acoustic isolation chamber in order to secure a vibration-free analysis environment. The secondary electron imaging and Auger signal imaging spatial resolutions are 6 nm and less than 7 nm, respectively, with an electron beam of 1 nA, 20 kV. We have examined Auger observations of cross-sectional surfaces of epitaxially grown GaAs/AlAs superlattice systems with this instrument. It was easy to obtain Auger elemental mapping showing the GaAs(10 nm)/AlAs(10 nm) structure. Generally speaking, Auger signal intensity is in proportion to the atomic density for the element of interest. Although the atomic densities of As atoms in GaAs and AlAs are almost the same, the As intensity from a GaAs layer is extremely different from that from an AlAs layer. Its intensity, defined as peak-to-peak strength in differential spectra, from GaAs layers is twice as strong as that from AlAs layers. It was also found that the Al peak shape gradually changes from the interface with GaAs layer to the center of AlAs layer, though the Ga peak shape does not change at the center of GaAs layer and at the interface. In the presentation, we will detailedly discuss the sensitivity factors in GaAs and AlAs layers and chemical state variation across the cross-sectional multilayer surface.

12:20pm **EW-WeL2 Ultimate Nanoprobing in UHV: Four Independent Scanning Tunneling Microscopes Navigated by High Resolution UHV SEM***, **M. Maier**, J. Westermann,* OMICRON NanoTechnology GmbH, Germany

A main challenge in Nanotechnology is the integration of single nano-devices into large integrated circuits. Device technologies require high resolution topographical and chemical analysis with well established experimental techniques or electrical characterization using standard probing systems. Nevertheless, typical instrumentation lacks from one fundamental problem: Bridging dimensions of a fully integrated circuit down to the nanometer range (or even atomic scale) of single devices by using an adequate integrated navigation system. Moreover, sensitive nano-devices require ultra clean conditions, a goal which is best achieved under true UHV conditions. To meet these new requirements, we have established a new approach integrating state-of-the-art SPM technology with high resolution electron microscopy and spectroscopy: (1) Bridging dimensions and rapid navigation; (2) Combining different surface analysis methods at the very same sample area to gain complementary information; (3) Pushing each single technology to its inherent limits. The UHV NANOPROBE facilitates four independent Scanning Tunneling Microscopes, each one equipped with 3D coarse positioning and full STM capability. A UHV Gemini SEM column with ultimate resolution down to 3nm is used for probe navigation and rapid localization of sample features or devices. STM imaging is engaged to exactly position the local probe. Using STM probe approach technology, a controlled electrical contact is ensured to finally perform a four-point measurement on the nano-scale. Beyond that, the UHV Gemini SEM column itself has unsurpassed performance: Low beam energies down to 100eV avoid sample damage and makes imaging on insulators possible. Beam currents up to 10nA make this electron source an ideal base for high resolution chemical analysis with Scanning Auger Microscopy below the 10nm benchmark.

12:40pm **EW-WeL3 Advances in Nanoindentation and Application to Ultra-Thin DLC Films***, **J.M. Burkstrand**, S. Downs,* Hysitron, Inc.*; J.F. Moulder,* Physical Electronics, USA

Recent trends in miniaturization of devices and demands for high-performance materials dictate a change in the way that materials are characterized. Understanding of the structure, properties and role of processing at the nanoscale is crucial to achieving the desired performance, regardless of the size scale of the final product. Nanomechanical characterization is a relatively new solution for materials testing, expanding on the range of capabilities of traditional hardness testing. Nanoindentation provides superior lateral and vertical resolution, allowing testing of surface properties or single phases of multi-phase materials. Typical nanoindentation and nanoscratching provide measurement of mechanical properties such as modulus, hardness, fracture toughness, friction coefficients and wear resistance. Hysitron has developed a new technique called modulus mapping which measures the spatial variation of a materialâ?Ts modulus in the near surface region. This nondestructive testing technique has been applied to very thin DLC films, <3 - 10nm, used in the storage industry and has produced some very interesting and exciting results. The modulus maps can quickly distinguish different areas with dissimilar mechanical properties which result from variations in deposition. A more complete picture of the ultra-thin properties emerges when these results are combined with other nanoindentation results and with XPS depth profiles of the same materials.

1:00pm **EW-WeL4 Nano-structuring and Nano-manipulation with Scanning Probe Microscopy***, **S. Wu**,* Molecular Imaging

Nanotechnology extends to all areas of research, from nanodevices to single molecular interactions. Scanning Probe Microscopy provides the perfect tool for nanostructuring and nanomanipulation, so that components such as nanoparticles, nanowires, atoms, and molecules can be analyzed and engineered to nanodevices for applications such as nanoelectronics, drug delivery and disease diagnoses. Molecular Imaging has invested more than 10 years of innovative research in the development of advanced scanning probe technology for controlled environments such as atmosphere, fluid and temperature. The workshop will focus on the application of PicoSPM® system in nanostructuring and nanomanipulation. Nanostructuring will demonstrate examples from both mechanical and electric lithography. Nanomanipulation will discuss examples of pushing and aligning of nanoparticals and nanowires. The study of electronic properties of single molecular wires, and conductive properties of thin films such as self-assembled monolayers with current sensing techniques will also be covered. An in depth review of PicoTREC@super TM@ will be presented. PicoTREC allows simultaneous imaging and mapping of single molecule interactions. Using PicoTREC, reasearchers can quickly distinguish between species that are engaged in molecular binding events and those that are not engaged in molecular binding events thus eliminating the need to perform slow and tedious force spectroscopy experiments to get the same results. It is now possible to conduct molecular recognition experiments with AFM easily and to get results in less time. Scientists can explore dynamic properties of biological systems such as antibody-antigen, ligand-receptor, drug-receptor, DNA-protein, and DNA-DNA.

1:20pm **EW-WeL5 Recent Developments in Scanning Probe Microscopy***, **M. Serry**,* Veeco Instruments

This workshop will introduce new and inventive scanning probe microscopy (SPM) technology including the Digital Instruments EnviroScope that combines modular environmental controls, a sealed hermetic sample chamber, and a wide range of imaging modes to bring superior application flexibility to research and industrial facilities. The EnviroScope allows SPM experiments to be conducted in air, vacuum, and fluid with environmental control. We will also review basic and advanced SPM techniques including force spectroscopy, nanolithography and nanomanipulation, scanning thermal microscopy, and liquid imaging using the Digital Instruments CP-II SPM. These advanced techniques are continuing to be vital to both researchers and educators in the material, physical and life science research areas. The CP-II SPM combines closed-loop scanning, integrated high-magnification color optics, and an intuitive graphical user interface to offer a powerful and easy-to-use scanning probe microscope.

Applied Surface Science
Room 210A - Session AS+BI-WeA

Biological Applications of Surface Analysis

Moderator: A. Belu, Medtronic

2:00pm **AS+BI-WeA1 G-SIMS-MS: Towards Molecular Structure at Surfaces***, **I. Gilmore**, F. Green, M. Seah,* National Physical Laboratory, UK

SSIMS is a powerful technique for the analysis of complex surfaces. However, many view SSIMS as an excellent research tool but unreliable as an analytical method. This is changing. Modern instruments have superb repeatability and reliability. In the VAMAS 2002 SSIMS inter-laboratory study, the average repeatability of 27 instruments was already 2%. Accessibility to SSIMS measurements is increasing rapidly. However, the complexity of mass spectra makes identification and quantification far from straightforward, even for the experts! This is a major barrier to the wider take-up of SSIMS, especially in new fields. One way around this problem is G-SIMS. G-SIMS or gentle SIMS is a library independent method providing a straightforward way to simplify SSIMS spectra@footnote 1 @@footnote 2 @@footnote 3 @. SSIMS spectra are composed of parent fragment ions amongst a large number of high intensity degradation products. In G-SIMS, this fragmentation may be quantified in terms of the partition functions of the fragments emitted from a surface plasma with effective temperature, T@sub p@. By extrapolation of the data to low T@sub p@, the intensity of the degradation products rapidly reduces, revealing the parent fragments. The latter peaks are directly characteristic of the material without rearrangement and can enable direct interpretation and identification. This is fine for smaller molecules but, within the plethora of possible larger molecules for which a total mass is insufficient to provide adequate characterisation, an extension of G-SIMS has exciting prospects to elucidate the required structure. Here we use, G-SIMS-MS, to explore the re-building of parent molecules using the fragmentation pathways that are mapped out as T@sub p@ is varied. @FootnoteText@ @footnote 1@ I S Gilmore and M P Seah, Appl. Surf. Sci., 161 (2000) 465. @footnote 2@ I S Gilmore and M P Seah, Appl. Surf. Sci., 187 (2002) 89. @footnote 3@ I S Gilmore and M P Seah, Appl. Surf. Sci., 203-204 (2003) 551.

2:20pm **AS+BI-WeA2 Functional Molecular Surfaces for Healthcare - Characterisation, Analysis and Understanding***, **M.C. Davies**, S.J.B. Tender,* University of Nottingham, UK*; P.M. Williams,* University of Nottingham, UK, U.K.*; C.J. Roberts, S. Allen,* University of Nottingham, UK **INVITED**

The characterisation of the surface structure of both conventional and advanced biomedical systems can be an important step in understanding the performance and optimising the function of such healthcare devices. A number of advanced biophysical analytical techniques have emerged for the study of pharmaceutical and biomedical systems. In this talk, we shall explore the role of these analytical tools as complimentary techniques, in the study of surface structure and function of advanced polymeric materials. The value and limitations of visualisation of surface topography and morphology of polymeric devices will be discussed and will include the condensation of polymeric constructs for gene therapy to the single molecule imaging of micro-patterned proteins on nanoengineered tissue-engineering substracts. The role of the force microscope in determining interparticulate and inter-molecular forces in order to explore its potential for the study of biomolecular interactions at polymer interfaces through to the macromolecular stimuli response hydrogels will be reviewed. The potential of the biophysical methodology of high-resolution imaging and force spectroscopy to aid research in biorecognition, development of gene delivery systems and understanding interparticulate and molecular forces, will be highlighted. The ability to identify the chemical structure of the molecules laterally across of a surface for both model and complex multiplayer patterned macromolecular assemblies shows promise but faces major challenges to low surface density ligands and high throughput array systems. The need for new approaches for handling large data sets of surface information and their relationship to surface functionality remains a significant challenge. The talk will aim to provide an objective assessment of current status, future challenges and opportunities.

3:00pm **AS+BI-WeA4 Model Calculations for the Quantification of XPS-Results; Application to Self Assembled Monolayers on Gold***, **C. Van der Marel**, J.H.M. Snijders, H.R. Stapert,* Philips Research, The Netherlands

XPS-analysis is widely applied for the characterization of surfaces and multilayers of thin films. In order to obtain quantitative results, the XPS peak areas generally are divided by appropriate sensitivity factors and normalized to 100 at% to obtain the apparent concentrations. Within the model developed by us, the sample is assumed to consist of a substrate on top of which a number of homogeneous layers are present. Starting from the apparent concentrations, the model calculation provides the thickness, the number of sulphur atoms per surface area and the composition of all layers. The proposed method requires only one measurement at one measuring angle to obtain these results. The method has been verified for a large series of self assembled monolayers made of mercaptoalkyl-polyethylene glycol compounds with various chain lengths on gold-plated Si. The influence of deposition time upon the obtained SAM-layers was examined; also SAM-layers deposited from mixtures of molecules with different chain length were investigated. RBS analysis was applied to determine in an independent way the amount of sulphur at the gold surface (expressed in number of Sulphur atoms per unit area); the RBS results correlated well with the XPS data. Also XPS-results obtained from mixtures of mercaptodeca-triethylene glycol and biotinylated thiols were analyzed in this way. The method resembles the calculation method proposed recently by Petrovykh et al@footnote 1@. Yet, in the latter method the analysis is restricted to only one layer on top of a substrate. Moreover, ion-etching is required to obtain a reference signal of the gold substrate; the consequence is, that elastic scattering of Au4f-electrons in the top layer is partly neglected in Ref.@footnote 1@. @FootnoteText@ @footnote 1@ D. Y. Petrovykh, H. Kimura-Suda, M.J. Tarlov and L.J. Whitman, Langmuir 20 (2004) 429.

3:20pm **AS+BI-WeA5 Surface Analysis by Friction Force Microscopy***, **G.J. Leggett**,* University of Sheffield, UK*; N.J. Brewer,* Dundee University, UK*; K.S.L. Chong,* University of Sheffield, UK

The characterisation of surface chemical structure on the nanometre scale still presewnts significant challenges. Friction force microscopy (FFM) is a widely accessible technique typically provided as standard on commercial atomic force microscoopes. It is capable of providing significant insights into variations in surface chemical composition and molecular organisation. The sensitivity of FFM to changes in molecular organisation will be illustrated with data from studies of self-assembled monolayers (SAMs) on Au and Ag. It will be shown that unexpected packing density differences, revealed by FFM, correctly predict the variation in the photo-oxidation kinetics of these materials. FFM suggests that while SAMs of methyl temrinated adsorbates on Ag are more closely packed on than they are on Au, the reverse is the case for monolayers of carboxylic acid terminated thiols. Methyl terminated SAMs on Ag oxidise more slowly than similar monolayers on Au, while the reverse is true for carboxylic acid terminated SAMs, reflecting the strong influence of molecular packing on photo-oxidation kinetics. The kinetics of SAM photo-oxidation have also been studied and quantified by FFM. Samples of carboxylic acid terminated thiols were exposed to UV light for varying periods of time and then immersed in solutions of methyl terminated thiols. Oxidised adsorbates were replaced by solution-phase thiols. For macroscopic samples, the variation in the coefficient of friction determined by FFM as a function of SAM photo-oxidation correlates closely with the variation in the contact angle (ie, as oxidation proceeds the SAMs become increasingly hydrophobic, and exhibit an increasingly small coefficient of friction). Similar types of analysis may be used to quantify rates of reactions in photopatterned materials SAMs. For materials with structures as small as a few tens of nm, fabricated by scanning near-field optical lithography, FFM enables the monitoring of chemical reactivity.

3:40pm **AS+BI-WeA6 Synthesis, Characterization and Modeling of Tethered Poly (N-isopropylacrylamide)***, **S. Mendez**, G.P. Lopez,* The University of New Mexico*; H. Yim, M.S. Kent, J.G. Curro,* Sandia National Laboratories*; J.D. McCoy,* New Mexico Tech

Tethered polymers are widely used to control surface properties such as adhesion and wettability. By making thin films out of polymers that are thermo-responsive, we can modulate surface properties with changes in temperature. Specifically, we use poly(N-isopropylacrylamide) (PNIPAM) since this exhibits lower critical solution temperature (LCST) behavior near 32 degrees Celsius in water. At temperatures below the LCST, the polymer is hydrated and swollen, whereas above the LCST, the polymer collapses, and when tethered, the surface becomes more hydrophobic. We report a method of growing PNIPAM from mixed self-assembled monoloyers (SAMs) using atom transfer radical polymerization. The use of two-component SAMs with varying composition permits for the control of polymer surface coverage, and the molecular weight can be controlled by the polymerization time. We have used both surface plasmon resonance and neutron reflectivity techniques to make direct measurements of the polymer brush structure at temperatures above and below the solution LCST. The effects of polymer surface coverage and molecular weight on the polymer structure were investigated. To model the temperature-induced structural changes of these brushes, we employed self-consistent field (SCF) theory using as input the chi parameter extracted from the experimental polymer solution phase diagram. The brush structure as predicted by SCF theory is in qualitative agreement with experimental data.

4:00pm **AS+BI-WeA7 Reversible Control of Free Energy and Topography of Nanostructured Surfaces***, **Q. Fu**, G.V. Rama Rao, S.B. Basame, D.J. Keller, K. Artyushkova, J.E. Fulghum, G.P. Lopez,* The University of New Mexico

We describe a facile method for the formation of dynamic nanostructured surfaces based on the modification of porous anodic aluminum oxide with poly(N-isopropyl acrylamide) (PNIPAAm) via surface-initiated atom transfer radical polymerization. These hybrid membranes were characteriazed by FTIR, TGA, SEM. The dynamic structure of these surfaces was investigated by atomic force microscopy (AFM), which showed dramatic changes in the surface nanostructure above and below the aqueous lower critical solution temperature of PNIPAAm. These changes in surface structure are correlated with changes in the macroscopic wettability of the surfaces, which was probed by water contact angle measurements. Principal component analysis was used to develop a quantitative correlation between AFM image intensity histograms and macroscopic wettability. Such correlations and dynamic nanostructured surfaces may have a variety of uses.

4:20pm **AS+BI-WeA8 Characterization of Bound Nucleotides using XPS and ATR-FTIR***, **D.B. Barbash**, J.E. Fulghum, G.P. Lopez, Y. Wu,* The University of New Mexico

In this work we utilize XPS and ATR-FTIR to probe the attachment of nucleotides to self-assembled monolayers. The attachment of DNA onto functional surfaces is utilized in applications ranging from DNA microarray technology to molecular wires. We are utilizing nucleotides as model systems in the development of surface-specific methods for the analysis of bound DNA. The nucleotides or DNA are covalently bound to self-assembled monolayers on glass or gold substrates using a diazotization-based method we recently developed (Dolan, P.L. et al. Nucleic Acids Research 2001, 29, 21e107). Three of the four nucleotides can be attached using this method, and we report unique spectral signatures for the nucleotide bases adenine (dATP), cytosine (dCTP), and guanine (dGTP) based on ATR-FTIR and XPS analyses. Based on these spectral signatures, results of competitive binding experiments will be discussed. XPS is also utilized to characterize the attachment steps and estimate surface coverage. ARXPS results of bound nucleotides will be discussed.

Biomaterial Interfaces
Room 210D - Session BI-WeA

"Passive" and Non-Fouling Surfaces

Moderators: H.J. Griesser, University of South Australia, T.A. Horbett, University of Washington

2:00pm **BI-WeA1 PEG Modified Trichlorosilanes as Protein Repellent Coatings for Oxide Surfaces***, **R. De Palma**,* IMEC, Belgium*; K. Jans,* KULeuven, Belgium*; K. Bonroy, W. Laureyn,* IMEC, Belgium*; G. Maes,* KULeuven, Belgium*; C. Van Hoof,* IMEC, Belgium

The construction of oxide based microelectronic devices interfaced with biological components requires methods for assembling biomolecules on their surfaces in a controlled manner. Examples include biosensors, chip-based diagnostic assays and biomaterials used for implants and tissue engineering. A key issue in the design of analytical devices which contact biomolecules is that non-specific adsorption of biological species, particularly proteins, can limit their performance. Surface-bound poly(ethyleneglycol) is a powerful reagent to construct protein repellent surfaces on various substrates. Most procedures reported to yield PEG layers on oxides require several steps and thus decrease the surface controllability. To overcome the problems encountered during PEG surface modification, we have synthesized novel reagents which combine the silane surface modification properties and the protein resistant properties of short PEG (@<=@ 6) units to generate robust coatings for glass and metal oxides. Tantalum was used as a substrate because of the high chemical stability of its thin passivating oxide and was found to play an important role in the silane SAM formation. The molecular architecture of the deposited silane layers and the PEG chain conformation was studied using contact angle measurements, XPS, AFM, RAIRS, LDI-TOF-MS and ellipsometry. The non-specific adsorption of human serum and its 4 most abundant proteins were elaborated using quartz crystal microbalance with dissipation monitoring (QCM-D) and confocal fluorescence microscopy. The protein repellent properties of the PEG silane SAMs were shown to be strongly correlated to the PEG chain length and their molecular architecture. The correlation between the PEG length and the viscoelastic properties of the adsorbed protein film have led to a better insight into the phenomenon of protein repellence. Future work will involve the deposition of mixed PEG silane SAMs to further improve the protein resistant properties.

2:20pm **BI-WeA2 The Effect of Cloud-Point Grafting of Sulfonated Poly(ethylene glycol) on Albumin Adsorption***, **L.G. Britcher**, H.J. Griesser,* University of South Australia, Australia*; Y.H. Kim,* Korea Institute of Science and Technology

Sulfonated poly(ethylene glycol) (PEG-SO@sub 3@) has shown promise as a thromboresistant material, although its activity does reduce when grafted onto a polyurethane surface. It is thought that a synergistic effect exists between the PEG and terminal SO3 groups, improving its blood compatibility@footnote 1@. The flexible hydrophilic PEG chains cause protein rejection by a steric barrier mechanism, while the negative charge of the SO@sub 3@ terminal groups causes electrical repulsion of negatively charged proteins and platelets@footnote 1@ @super ,@@footnote 2@. Though platelet adhesion is decreased on PEG-SO@sub 3@ grafted surfaces compared with PEG grafted surfaces, protein adsorption is not suppressed completely. A negative cilia adsorption model has been proposed for these surfaces, however, it does not explain why albumin adsorption is enhanced. Therefore, further work is required in order to understand what conformation of the PEG-SO@sub 3@ on the surface along with the distribution of SO@sub 3@ groups will lead to improved anti-fouling properties. One method for changing the PEG conformation is to use cloud point conditions for grafting the PEG. Surfaces grafted under these conditions have shown to decrease protein adsorption significantly, as the coating is very dense due to the brush conformation of the PEG@footnote 3@. However, charge repulsion effects may arise with densely packed sulfonated PEGs. In this study, we aim to investigate whether cloud point conditions can be used to graft PEG-SO@sub 3@ onto surfaces and if the coating thus obtained suppresses albumin adsorption. This should lead to further understanding of the protein adsorption model on PEG-SO@sub 3@ surfaces. @FootnoteText@ @footnote 1@ Y. Hann et al., Biomaterials 24, 2213 (2003).@footnote 2@ H. Lee et al., Colloid Surf B: Biointerfaces 18, 355 (2000).@footnote 3@ P Kingshott et al., Biomaterials 23, 2043, (2002).

3:00pm **BI-WeA4 Biologically Inspired Peptide-Mimetic Polymers for Prevention of Cell and Protein Fouling***, **P.B. Messersmith**, A.E. Barron, J.L. Dalsin, A. Statz, R.J. Meagher,* Northwestern University **INVITED**

The minimization of nonspecific interactions between biomolecules, cells and material surfaces is integral to refining the biological response biomaterials, and therefore is important to the success of numerous emerging healthcare technologies. A primary motivation for this study is the significant need for new nonfouling strategies capable of functioning effectively for long periods of time in-vivo, and which can be readily applied to a variety of material or device surfaces. In this talk, I will describe our ongoing research efforts aimed at developing new macromolecules that meet these criteria. Specifically, we are focusing on two key aspects of biomaterial surface modification related to prevention of protein and cell fouling: 1) the design and synthesis of new polymers capable of minimizing nonspecific protein and cell attachment to biomaterials; and 2) the development of robust and versatile approaches for anchoring these polymers onto biomaterial surfaces. We have synthesized new peptidomimetic polymers designed to be both fouling resistant and adhesive to surfaces. The anchoring component of the polymers is inspired by the adhesive proteins secreted by mussels for attachment to marine surfaces, whereas the nonfouling polymer is either poly(ethylene glycol) (PEG), or a poly(N-substituted glycine) (polypeptoid). Polypeptoids offer the advantages of resistance to enzymatic degradation, low immunogenicity, and with proper design, the ability to prevent protein and cell attachment at surfaces. The synthesis and characterization of these peptidomimetic polymers will be described, along with evidence for their surface immobilization and performance as antifouling coatings.

3:40pm **BI-WeA6 Stable Protein-resistant Surfaces: Covalent Immobilization of Poly(L-Lysine)-g-Poly(Ethylene Glycol) onto Plasma-modified, Aldehyde-activated Substrate Surfaces***, **T.M. Blättler**, S. Pasche, M. Textor,* Swiss Federal Institute of Technology, Switzerland*; H.J. Griesser,* University of South Australia, Australia

The fabrication of protein resistant surfaces is of considerable interest for a number of applications. Electrostatically adsorbed PEGylated graft copolymers, such as poly(L-lysine)-g-poly(ethylene glycol) (PLL-g-PEG), have been very successful in reducing protein adsorption on negatively charged metal oxide surfaces. The drawback is their instability under extreme conditions (extreme pH or high ionic strength). We have overcome this limitation in the present work by covalently immobilizing PLL-g-PEG onto aldehyde plasma modified substrates. PLL-g-PEG was immobilized on silicon wafers in two consecutive steps: First the silicon wafer was coated with a propionaldehyde plasma polymer layer (AHPP); secondly, the PLL-g-PEG was immobilized covalently by reacting part of the amine groups of the PLL backbone with the aldehyde groups present on the plasma-deposited polymer layer (reductive amination). The stability and the protein resistance of different architectures of PLL-g-PEG were quantitatively investigated by XPS, OWLS and ToF-SIMS. Protein resistance of the polymer-modified surfaces was tested against bovine serum albumin (BSA). Adsorption of BSA was below the detection limit (below 2 ng/cm@super 2@), similarly to the electrostatically adsorbed PLL-g-PEG. However, after 24 h exposure of the covalently immobilized PLL-g-PEG to high ionic strength buffer (2400 mM NaCl) no significant change in the protein resistance was observed, while under the same conditions electrostatically adsorbed PLL-g-PEG coatings lost their protein resistant properties. These findings provide good evidence for the covalent nature of the PLL-g-PEG binding to the surface. This work has created a general platform for the covalent immobilization of PLL-g-PEG onto a wide variety of substrates provided that they are compatible with the AHPP coating process.

4:00pm **BI-WeA7 Control of Protein Adsorption Using Poly(propylene sulfide)-block- poly(ethylene glycol) Adlayers: New Potential Candidate for the Modification of Biosensor Chip Surfaces***, **L. Feller**, S. Tosatti,* Swiss Federal Institute of Technology (ETHZ), Switzerland*; S. Cerritelli, S. Terrettaz,* Swiss Federal Institute of Technology (EPFL), Switzerland*; M. Textor,* Swiss Federal Institute of Technology (ETHZ), Switzerland*; J.A. Hubbell,* Swiss Federal Institute of Technology (EPFL), Switzerland

Poly(ethylene glycol) (PEG) has been used in numerous biomedically relevant systems to aid in the minimization of protein adsorption and cell adhesion. PEG can be attached to surfaces through a variety of different approaches including silanization, self-assembly of thiols, and plasma polymerization. In our approach a block copolymer containing one (di-block) or two (tri-block) PEG chains separated by a poly(propylene sulfide) (PPS) part was used. Adsorbed to gold surfaces, a stable linkage between the sulfur atoms of the PPS thioether and the metal surface was observed. The hydrophilic PEG part formed a dense layer of biocompatible PEG chains, which is exposed to the aqueous environment. Various architectures of di- and tri-block PPS-PEG copolymers were synthesized, characterized, and deposited on gold substrates. While the PPS part was kept constant (MW 4000), the PEG part was varied between 1100 and 5000 Da molecular weight. Adsorption of the polymer to the gold surface was characterized by ex situ ellipsometry, X-ray photoelectron spectroscopy (XPS), and in situ surface plasmon resonance (SPR). The resistance of the surfaces to protein adsorption was evaluated using SPR. PPS-PEG readily chemisorbed on gold surfaces after a simple dip-and-rinse process in 1mg/ml methanol solution. We compared different architectures of PPS-PEG and correlated the PEG/PPS ratio with adsorbed mass values and resistance to protein (HSA) adsorption with the aim to find the optimum architecture regarding surface adhesion, stability, polymer conformation and protein resistance.

4:20pm **BI-WeA8 Surface Segregation of Pluronic® P104 in Poly(@subL@-lactic acid) Characterized by XPS and ToF-SIMS***, **J.-X. Yu**,* State University of New York at Buffalo*; C.M. Mahoney,* National Institute of Standards and Technology*; J. Gardella,* State University of New York at Buffalo

This study reports results of the surface and in-depth characterization of two component blend films of poly(L-lactic acid) (PLLA) and Pluronic® surfactant [poly(ethylene oxide) (A) poly(propylene oxide) (B) ABA block copolymer]. The bulk properties of these polymers have been well studied by many groups due to their biomedical applications. Angle dependant X-ray photoelectron spectroscopy (XPS) and Time-of-flight secondary ion mass spectrometer (ToF-SIMS) depth profiling were used for monitoring the surfactant's surface concentration at different sampling depths. We found a critical saturation concentration of the surfactant, a depletion region beneath the topmost surfactant enriched zone, and the existence of the surfactant's segregation in the whole film with different intensities. We conclude that the surfactant's surface segregation increases and then stays stable when increasing its bulk concentration. These results suggest that the selection of the surfactant bulk concentration of the thin film matrices for drugs/proteins delivery should achieve a relatively homogeneous distribution of stabilizer/protein in the PLLA matrix.

4:40pm **BI-WeA9 Heterobifunctional PEG Tethered Chains Surface - Preparation, Physicochemical and Biochemical Properties***, **Y. Nagasaki**, K. Uchida,* Tokyo University of Science, Japan*; H. Otsuka, K. Kataoka,* The University of Tokyo, Japan **INVITED**

In the case of microanalysis in a crude sample such as serum, nonspecific adsorption of various proteins and lipids to the surface is an important consideration to achieve specific biosensing with high S/N ratio. In order to avoid the nonspecific adsorption, many types of modification on the sensor surface have been considered. Modification by poly(ethylene glycol) (PEG) tethered chains leads to reduce the nonspecific interaction of biomolecules such as proteins and cells with biomedical devices because PEG is a nontoxic and hydrophilic polymer with low interfacial free energy in water and high-chain mobility inducing excluded volume effects. In this paper, we are focusing on preparation of complete non-fouling surface by mixed PEG tethered chain, which denotes the introduction of short under-brushed PEG layer to the surface pre-modified with comparatively long PEG chain resulted. By using our original heterotelechelic PEG, which means PEG having a functional group at one end and another functional group at the other chain end quantitatively, ligand-installed non-fouling surface was constructed. In the case of dextran gel as a control, non-specific adsorption was avoided to some extent in the case of high molecular weight protein. With decreasing the size of the protein, the non-specific adsorption increased significantly. The conventional PEG tethered chain surface suppressed the non-specific adsorption of the proteins possessing the molecular weight higher than 10kD. However, it is not enough performance for the protein lower than 10kD. In the case of the mixed PEG tethered chain surface, complete non-fouling character was observed. Especially, the mixed PEG tethered chain avoided tetrapeptide (RGDS, MW=450), which is anticipated as ideal biomateials surface.

Magnetic Interfaces and Nanostructures
Room 304A - Session MI-WeA

Exchange Coupling, Surfaces, and Interfaces

Moderator: M.E. Hawley, Los Alamos National Laboratory

2:00pm **MI-WeA1 Spin-Dependent Quantum Size Effects in Ultrathin Co Single Crystals***, **R. Zdyb**, E. Bauer,* Arizona State University

We have prepared micron-sized ultrathin (0001)-oriented Co single crystals with thicknesses varying between 1 and 10 monolayers by epitaxy on W(110) and studied the spin-dependent reflectivity of electrons with energies up to about 20 eV in spin-polarized low energy electron microscope. Similar to our previous study of ultrathin (110)-oriented Fe single crystals@footnote 1@ , quantum size effects allow the determination of the exchange splitting of the sp band above the vacuum level. We will also report the results of our attempts to understand the apparent oscillatory spin reorientation transition in ultrathin Co films@footnote 2@. @FootnoteText@ @footnote 1@ R. Zdyb and E. Bauer, Phys. Rev. Lett. 9 (2002) 1485. @footnote 2@ T. Duden and E. Bauer, Phys. Rev. Lett. 77 (1996) 2308.

2:20pm **MI-WeA2 Electronic Resonances of Isolated Mn and Interacting Mn-Mn Complexes on GaAs (110) Surfaces@footnote 1@***, **A. Richardella**, D. Kitchen, A. Yazdani,* University of Illinois at Urbana-Champaign

Using low temperature scanning tunneling microscopy (STM) Mn on GaAs (110) surfaces has been studied. We present results for isolated Mn adatoms evaporated at low temperature on in situ cleaved n-type and p-type GaAs substrates. Localized modifications of the density of states of the substrates due to Mn are shown. Isolated Mn adatoms can exhibit two equivalent stable bonding states which STM atomic manipulation can induce transitions between. Additionally, certain tunneling parameters lead to increased mobility of Mn on the surface. It is shown isolated Mn's display a strong preference to pair along certain lattice directions. This pairing presents a unique opportunity for studying the interaction of magnetic impurities mediated through the underlying semiconductor states. Resonances due to these Mn-Mn interactions are presented using local density of states (LDOS) spectra and energy resolved spatial maps. In particular it is shown that similarly spaced Mn-Mn pairs can exhibit a number of distinct localized electronic resonances. Studies are ongoing into whether these varied localized states result from the relative spin orientations of the impurities with respect to each other and the surface. @FootnoteText@ @footnote 1@ This work was supported by ARO MURI DAAD19-01-1-0541.

2:40pm **MI-WeA3 Non Linear Aspects of Ultrathin Film Magnetism*, D. Pescia*,** *O. Portmann,* ETH Zurich, Switzerland*; M. Buess,* University of Regensburg, Switzerland*; A. Vaterlaus,* ETH Zurich, Switzerland*; C.H. Back,* University of Regensburg, Switzerland **INVITED**

We report on two experiments. In the first one, the stripe phase of perpendicularly magnetized ultrathin films is shown to form a Mermin-like 2D solid with algebraic correlations. The second one consists in exciting the spin motion in a vortex-like spin configuration by an ultrashort magnetic field pulse and imaging the local spin dynamics with pico-second time resolution. Both experiments reveal new non-linear aspects of ultrathin film magnetism.

3:20pm **MI-WeA5 Overcoming Thermal Fluctuations in Ferromagnetic Nanostructures using Exchange Bias*, J. Nogués*,** Inst. Catalana de Recerca i Estudis Avancats, Spain, Sapin*; V. Skumryev,* Inst. Catalana de Recerca i Estudis Avancats, Spain*; S. Stoyanov, Y. Zhang, G. Hadjipanayis,* U. of Delaware*; D. Givord,* CNRS-Grenoble, France*; K. Liu,* U. of California-Davis*; C. Leighton,* U. of Minnesota*; H. Masuda, K. Nishio,* Tokyo Metro. U., Japan*; I.V. Roshchin, I.K. Schuller,* UCSD*; J. Eisenmenger,* U. Ulm, Germany*; J. Sort, J.S. Muñoz, S. Suriñach, M.D. Baró,* U. Autònoma de Barcelona, Spain **INVITED**

Today's interest in nanoparticle magnetism is stimulated by a variety of potential applications, ranging from ultra-high density information storage to medicine. Most applications rely on the magnetic order of the nanoparticles being stable with time. However, in small particles, thermal fluctuations may affect the magnetization stability and possibly lead to superparamagnetism. In this study, we will demonstrate that the exchange coupling between ferromagnetic (FM) nanostructures and antiferromagnetic (AFM) hosts can lead to the magnetic stabilization, i.e. enhancement of coercivity (H@sub C@), increase of remanence (M@sub R@) and ultimately improvement of the superparamagnetic blocking temperature (T@sub B@). Three different cases will be discussed: (i) Co particles ball milled with NiO@footnote 1@, where a small increase of the coercivity and the remanence is observed. (ii) Fe nanostructures deposited on FeF@sub 2@ layers@footnote 2@, where a clear enhancement of the remanence of the hysteresis loop is seen and appears to be linked with its coercivity enhancement. (iii) Co nanoparticles embedded in CoO@footnote 3@, where the blocking temperature is substantially improved with the concomitant increase of H@sub C@ and M@sub R@. In particular, 4nm-Co particles, embedded in a CoO matrix, remain ferromagnetic up to the Néel temperature of CoO. This corresponds to almost 30-fold increase in the blocking temperature compared to the uncoupled nanoparticles. The AFM-FM coupling can be viewed as providing an extra source of anisotropy, thus leading to magnetization stability. @FootnoteText@ @footnote *@ Work supported by EU, CICYT and DGR (UAB), NSF, Seagate (UDEL) and US-DOE (UCSD)@footnote 1@ J. Sort et al., Appl. Phys Lett. 75, 3177 (1999)@footnote 2@ K. Liu et al., Appl. Phys Lett. 81, 4434 (2002)@footnote 3@ V. Skumryev et al. Nature 423, 850 (2003).

4:00pm **MI-WeA7 Growth and Study of Fe/Mn@sub 3@N@sub 2@(010)Bilayers for Use in Spintronics Applications*, R. Yang*,** *M.B. Haider, H.A. Al-Brithen, A.R. Smith,* Ohio University

Exchange biasing(EB)systems have drawn much attention in recent years, prompted by the intriguing physics and its prominent role in magnetic sensing devices.@footnote 1,2,3@ Yet, the detailed mechanism, which includes the spins at the ferromagnetic(FM)/antiferromagnetic(aFM)interface, is not fully understood. In this paper, we investigate the growth of an EB system using Fe/Mn@sub 3@N@sub 2@ (010) bilayers. The Mn3N2 (010) surface aFM magnetic structure is well understood by means of recent spin-polarized scanning tunneling microscope (SP-STM) studies.@footnote 4@ Mn@sub3@N@sub 2@ has a face-centered tetragonal(fct)rocksalt-type structure. The magnetic moments of the Mn atoms are FM within (001) planes, and are layerwise aFM along [001]. The Néel temperature of Mn3N2 is 925K.@footnote 4,5@ The next step is to study the initial stages of Fe growth on this surface. In this paper, we try to investigate the atomistic changes to the surface which occur at the initial stages of the growth. The growth begins with a 440 nm thick Mn@sub 3@N@sub 2@ aFM layer and substrate is MgO(001). After that, a small coverage (0-10ML) of Fe is deposited in different growth temperatures in the range 350-550@super o@C. The growth is monitored by reflection high-energy electron diffraction (RHEED). After growth, samples are transferred under ultra high vacuum (UHV) directly to STM analysis chamber . STM images reveal a stepped surface with terrace width about 50 Å . The dependence of the film properties on growth parameters such as growth temperature, film thickness and annealing time will be discussed. @FootnoteText@ @footnote 1@W. H. Meiklejohn, et al., Phys. Rev. 102,1413 (1956).@footnote 2@ C. L. Chien, et al., Phys. Rev. B 68, 014418 (2003).@footnote 3@ L. Ritchie, et al., J. Mag. Mag. Mater. 247, 187 (2002).@footnote 4@ H.Q. Yang, et al., Phys. Rev. Lett. 89, 226101 (2002).@footnote 5@ G. Kreiner, et al., J. Alloys Compd. 183, 345 (1992).

4:20pm **MI-WeA8 Magnetic and Structural Properties of Lattice Matched Epitaxial Antiferromagnetic/Ferromagnetic Bilayers*, P. Mani*,** *V.V. Krishnamurthy,* The University of Alabama*; S. Maat,* Hitachi Global Storage Technologies*; A. Kellock,* IBM Research Division*; G.J. Mankey,* The University of Alabama

The antiferromagnetism of FePt@sub 3@ films grown on Al@sub 2@O@sub 3@(11-20) and MgO(110) has been confirmed by neutron scattering. Fe@sub x@Pt@sub 1-x@ (0.2 < x < 0.3) exhibits antiferromagnetic ordering below 160K depending on the film growth temperature, substrate symmetry and composition of the alloy.@footnote 1@ These FePt@sub 3@ films offer a fascinating route to understand the relationship between structure and magnetism in exchange bias systems since Fe@sub x@Pt@sub 1-x@ grows as an ordered antiferromagnet when deposited at 750°C and as a disordered ferromagnet when deposited at 150°C. In addition, ferromagnetic films of CoPt@sub 3@ have the same lattice constant as FePt@sub 3@. Thus these film systems provide a pathway to create strain-free interfaces to test the current models of exchange bias. Both positive and negative exchange bias were observed in strained Fe/FePt@sub 3@ bilayers with different in-plane cooling field directions.@footnote 2@ In the present study, Fe@sub x@Pt@sub 1-x@ films are grown on MgO(111)and a-axis sapphire by co-sputtering Fe and Pt. Epitaxy and alloy ordering have been confirmed by x-ray diffraction. Rutherford backscattering spectrometry and energy dispersive analysis of x-rays were used to characterize the composition of these alloys, which confirms that stoichiometry can be controlled within a tolerance of 1% in our ultra clean sputtering system. Detailed measurements of the structural and magnetic properties of lattice matched FePt@sub 3@/Fe@sub 0.25@Pt@sub 0.75@ and FePt@sub 3@/CoPt@sub 3@ and their relation to current models of exchange bias behavior will be discussed. @FootnoteText@ @footnote 1@ S. Maat, O. Hellwig, G. Zeltzer et al., Phys. Rev. B, 63, 134426 (2001).@footnote 2@ R.L. Compton, M.J. Pechan, S. Maat, and Eric. E. Fullerton, Phys. Rev. B, 66 (5), 054411 (2002).

4:40pm **MI-WeA9 Momentum Transfer in Exchange Bias Systems of the Type F/af/aaf*, R. Mattheis*,** *K. Steenbeck,* IPHT, Germany

In F/AF exchange bias systems (F ferromagnet, AF antiferromagnet) momentum is transferred from the F film to the AF lattice by coupling via the AF interface net moment and the AF anisotropy. To study the dynamics of the AF lattice during rotation of the F layer magnetisation we sandwiched the F/AF system at the free AF side by a completely symmetric artificial antiferromagnet (AAF) of the kind CoFe/0.8 nm Ru/CoFe. At not too high magnetic field strength this AAF acts, due to its own coercivity and vanishing magnetic net moment, as a fixed spin system coupled at the opposite side of the AF. By means of torquemetry at 10K and 300K the rotational loss and exchange bias strength was determined for different AF thickness t. We found: a) The AAF can fix the AF spin system also at very low thickness t where K is zero. At this thickness exchange bias is found in F/AF system coupled to an AAF but not in the pure F/AF system. b) Fixing of the AF spins by coupling an AAF leads to a drastically reduction of the rotational losses in the AF and rotational anisotropy at a thickness where both where maximum without an AAF. The results show that overcoming the limited anisotropy in very thin AF films is possible by their coupling to an AAF. From the thickness dependence of the observed effects a deeper inside of the exchange bias phenomena is obtained and will be discussed in more detail.

5:00pm **MI-WeA10 Training in Exchange Bias Systems: The Role of Anisotropy*, A. Hoffmann*,** Argonne National Laboratory

The coupling between a ferromagnet and an antiferromagnet can give rise to a directional anisotropy called exchange bias. In order to establish the direction of the exchange bias, the coupled ferro-/antiferromagnetic system is generally cooled in the presence of an external magnetic field through the ordering temperature of the antiferromagnet. In many systems the magnitude of the exchange bias is reduced upon subsequent field cycling after the initial field cooling. These field-training effects are suspected to be due to irreversible changes in the magnetic microstructure of the antiferromagnet, but a comprehensive theoretical understanding is still missing. I will present numerical simulations based on a simple coherent rotation model, which suggest that the symmetry of the anisotropy in the antiferromagnet plays a crucial role for the understanding of these training effects. Namely, the existence of more than one antiferromagnetic easy anisotropy axes can initially stabilize a non-collinear arrangement of the antiferromagnetic spins, which relaxes into a collinear arrangement after the first magnetization reversal of the ferromagnet. This explains quite naturally why training effects are only observed for exchange bias systems with high symmetry antiferromagnets, while they are absent for antiferromagnets with uniaxial anisotropy. Furthermore, this simple and universal model reproduces many of the experimentally observed training effects. The model gives rise to a rotation of the effective easy axis for the ferromagnet after the first field reversal, such that the first magnetization reversal shows a large sudden jump, while all subsequent reversals are more gradual. I will compare in detail the calculated hysteresis loops with experimentally measured ones on the prototypical Co/CoO exchange bias system. This work was supported by the Department of Energy, Basic Energy Sciences under contract No. W-31-109-ENG-38.

Manufacturing Science and Technology
Room 303B - Session MS+AS-WeA

Non-Destructive Analysis and Metrology for Advanced Manufacturing

Moderator: A. Testoni, Varian Semiconductor Equipment

2:00pm **MS+AS-WeA1 Advances in X-ray Reflectivity (XRR) and X-ray Fluorescence (XRF) Measurements Provide Unique Advantages for Barrier and Metal Layer Measurements of 65 nm Node Devices**, *J.S. Spear,* Technos International*; H. Murakami,* ***S. Terada,*** Technos Company Limited, Japan

We have developed a thin-film metrology tool that fulfills the metrology requirements for the production of 65nm node technology and beyond. This tool combines X-ray Reflectivity (XRR) and X-ray Fluorescence (XRF) measurements to provide accurate, high throughput, measurements. Improvements in both the XRR and XRF configurations were made to allow high throughput measurements on films as thin as 0.5 nm. One of the challenges for the 65nm node is measuring the Cu metal layers and their accompanying barrier layers. The difficulty in measuring these layers is increased since the barrier is often a bi-layer composed of both TaN and Ta. This paper describes how a combined XRR XRF tool can be used to accurately measure these individual layers with optimum throughput.

2:20pm **MS+AS-WeA2 Non-Destructive Ultra-Thin Film (0-100A) Analysis in the Lab and the Fab.**, ***C.R. Brundle,*** C. R. Brundle and Associates **INVITED**

Whether for characterization or failure analysis work in the support laboratory, or for rapid quality control/metrology in a wafer processing fab, the need for analytical techniques capable of determining thickness, composition, and composition as a function of depth (including differences at interfaces) is increasing as the variety of film material used in processing expands, and as films and stacks get thinner. The current materials roster, and the stringency of analytical requirements are briefly reviewed, then four non-destructive techniques being deployed in lab and fab situations are discussed and their capabilities compared for these two different environments. They are X-Ray Fluorescence, XRF; X-Ray Reflectivity, XRR; X-Ray Photoelectron Spectroscopy, (XPS and angle resolved XPS); and Low Energy X-Ray Emission spectroscopy, LEXES.

3:00pm **MS+AS-WeA4 Crystalline Structure and Stress Characterization in Thin Films by Means of Optical Spectroscopy**, ***G. Conti,*** *Y. Uritsky,* Applied Materials, Inc.

Nondestructive characterization techniques are crucially important in developing new materials. Raman Spectroscopy is a powerful and versatile tool. Its capabilities range from structural identification and conformation of molecules, to identification of crystalline structure of materials. This power and versatility has led to its progressively more extensive applications to semiconductor industry as an analytical tool. In this paper we present some applications of Raman analysis to the characterization of thin films. The present challenge in thin films characterization is on one hand the determination of the film composition and/or crystalline phase; on the other the stress to which the film is subjected as it is deposited under different temperatures, chemical conditions of depositions, and substrates. In the first part, we report on the Raman characterization of silicides films generated on a Si surface. In particular we determine the stoichiometric composition of the silicides, their crystalline phase and their thickness. In the second part, we determine the stress of Si deposited on SiGe. The main advantage of Raman versus conventional X-ray diffraction is the ability to measure strain in thin layers (from 5 nm and above). We show here that Raman is the ideal method for characterizing strained cap Si layers with critical thickness in the range of 100-200 Å., and for characterizing stresses in quantum wires, quantum dots and other hetero-structures, which are becoming more and more important for fabricating devices with enhanced performance.

3:20pm **MS+AS-WeA5 Optical Properties (IR to VUV) and Birefringence of Graphite-like Amorphous Carbon**, ***S. Zollner,*** *R. Liu, R.B. Gregory, W. Qin, J. Kulik, N.V. Edwards, K. Junker,* Motorola*; T.E. Tiwald,* J.A. Woollam Co.

Amorphous carbon films of 50 nm thickness, low surface roughness, and low densities (1.5-1.7 g/cm@super 3@) were deposited on Si using plasma-enhanced chemical vapor deposition (PECVD) between 300 and 550°C. With increasing deposition temperature, the hydrogen content (determined with elastic recoil detection) is reduced from 35% to 15%. For films grown at lower temperatures, ellipsometry data (0.7 to 9.5 eV photon-energy range, taken at 35-75° angle of incidence on a rotating-analyzer ellipsometer with a computer-controlled Berek waveplate) can be fitted very well by a single optically isotropic layer with low visible absorption (@epsilon@@sub 2@1 Torr), the ion energy is expected to be very low, which leads to dominant sp@super 2@ character of our films@footnote 1@ (verified by electron energy loss spectrometry) and low density (

3:40pm **MS+AS-WeA6 Metrology for Advanced Manufacturing**, ***M.I. Current,*** Frontier Semiconductor **INVITED**

Metrology for process controls for manufacturing of advanced semiconductor devices faces an unprecedented number of challenges, well beyond the continued scaling to smaller transistors and denser functional arrays. Some common themes are the sharp increase in the introduction of new materials, new materials combination and interfaces and new device structures. This review will consider the metrology challenges and some new methods in four areas: (1) ultra-shallow doped junctions, including dopant activation and leakage currents, (2) stress and adhesion characteristics of metal/dielectric interfaces for gate and interconnect stacks, (3) local strain characterization of isolation structures, gates and channels as well as wafer-scale, strained materials systems and (4) bonding and layer transfer methods for integration of heterogeneous materials and devices such as, multi-level SOI wafers for logic, memory and photonic devices, 3-D packaging of functionally diverse devices and integration of MEMS/photonic structures with CMOS devices.

4:20pm **MS+AS-WeA8 Total Analysis of the Gases in Semiconductor Manufacturing Process: Use of Ion Attachment Mass Spectrometry**, ***M. Nakamura,*** *Y. Taneda, Y. Hirano, Y. Shiokawa,* ANELVA Technix Corporation, Japan*; M. Takayanagi, M. Nakata,* Tokyo University of Agriculture and Technology, Japan

Ion attachment mass spectrometry (IAMS)@footnote 1@ is a powerful tool to monitor semiconductor manufacturing process@footnote 2-3@ by analyzing the molecules in the gas because with IAMS fragment-free mass spectra can be obtained; i.e. only quasi-molecular ions without being suffered by dissociation are observed. The fragment-free detection is impossible with other ionization techniques such as the electron ionization. There are two-type equipments of IAMS; one for the process at the pressure from 100 Pa to atmospheric pressure, and the other for the process at several Pa. We analyzed the process for manufacturing semiconductor by measuring mass spectra of gases in the reaction chamber and of the exhaust gas simultaneously with these equipments. Very high frequency capacitively coupled plasma (VHF-CCP) (60 MHz, 1000 W) was produced in the reaction chamber by providing 2 Pa of Ar/c-C@sub 4@F@sub 8@/O@sub 2@ (100, 2, and 6 sccm, respectively). The equipment for gases at several Pa was installed on the sidewall of the reaction chamber with a connection pipe of 100-mm length. At the same time the exhaust gas from the reaction chamber was analyzed after the rough pump with the other IAMS equipment. Polymerized compounds such as carbonyl fluoloride (C@sub 4@OF@sub 8@, C@sub 5@OF@sub 10@, and so on) and other compounds were found not only in the exhaust gas@footnote 2@ but also in the reaction chamber. The kinds of compounds in the exhaust gas are less than those at the reaction chamber, suggesting the dissociation and the polymerization at the pumping line. We present in our talk about c-C@sub 4@F@sub 8@ plasma in other conditions, SiH@sub 4@ plasma, and other processes to show the applicability of IAMS. The authors are grateful to Dr. H. Ito et al. of ASET for their support to the experiments. @FootnoteText@ 1 T. Fujii, Mass Spectrom. Rev. 19, 111 (2000). 2 M. Nakamura et al., J. Vac. Sci. Technol. A 19, 1105(2001). 3 Y. Shiokawa et al., AVS Int. Sympo., PS-ThA1 (2003).

4:40pm **MS+AS-WeA9 Optimizing and Managing Calibration Gas Inventories to Address Accuracy, Analysis Shelf Life and the Cost of Ownership***, **P. Somssich**,* Osram Sylvania, Inc.

Today's analytical laboratories must meet ever-stricter quality controls and tracking requirements to maintain accreditation. Maintaining the usability of certified gas standards can be both time-consuming and costly. An ACCESS-based database was developed at Osram Sylvania Inc. to serve both cost management needs and the scientific requirements. The essentials of such a database required addressing critical issues: e.g., the shelf life of the certification, the traceability and cost of ownership. Almost 28 certified gas mixtures have since been recertified with initial fill and analysis dates going back 16 years. While some older mixtures were initially thought to be no longer useable, actual analysis results indicated that in most cases the vendor stated shelf life was far too short. However, there were a few dramatic exceptions. In addition to the costs associated with maintaining the certification, significant costs can occur by way of cylinder rentals, i.e., long term rental. This data is currently being evaluated to minimize the cost of ownership of the inventory, which includes 140 mixtures. The importance of good and accurate (or even very accurate) gas calibration standards has recently been highlighted by the use of EPA protocol gases associated with continuous emission monitors (CEMs). Since the Clean Air Act of 1990 makes the use of such monitors necessary, proper calibration standards and procedures can contribute to a sizeable financial windfall, while poor calibration can result in possible stiff penalties. Applications from lamp manufacturing will also be discussed showing a significant quality and financial benefit when lighting products are filled accurately resulting in optimal light output and performance as well as energy savings.

Nanometer-scale Science and Technology
Room 213D - Session NS-WeA

Nanotribology and Nanomechanics

Moderator: R.W. Carpick, University of Wisconsin-Madison

2:40pm **NS-WeA3 Qcm-Stm Study of the Nanotribology of Metal-Organic Interfaces***, **S.M. Lee**, M. Abdelmaksoud, J. Krim,* North Carolina State University

Energy transfer plays an important role in many surface processes such as surface diffusion, vibrational relaxation and sliding friction in adsorbed molecules.[1] The Quartz Crystal Microbalance has in recent years been employed to reveal much fundamental information on energy dissipation mechanisms associated with the sliding of atomically thin films along surfaces. While in quantitative agreement with theory and computer simulation, the QCM data have not been cross-referenced to scanning probe measurements of sliding friction and diffusive behavior of atoms along surfaces. We have thus combined a Scannning Tunneling Microscope and QCM to allow direct imaging of films adsorbed on the QCM electrode under both stationary and oscillating conditions.[2] In this study, the nano-scale frictional behavior of copper and nickel surfaces covered by various organic adsorbates (ethylene, iodobenzene, and etc.) was studied by means of STM-QCM. During the STM tip indentation, the changes in resonance frequency and amplitude of the quartz crystal were monitored simultaneously , to explore energy storage or loss mechanisms, as well as tribochemical effects, associated with tip-substrate interactions. The dependence of the frequency and the amplitude changes of each interface will be reported and interpreted in terms of the adsorbate-substrate chemical and physical interactions. Work supported by DOE, AFOSR and NSF. Reference: [1] J. Krim, Surf. Sci. 500, 741 (2002) [2] B. Borovsky, B. L. Mason, and J. Krim, J. Appl. Phys. 88, 4017 (2000).

3:00pm **NS-WeA4 Measurement of the Mechanical Adhesion between a Single-Walled Carbon Nanotube and a Silicon Dioxide Substrate***, **J. Whittaker**,* Brigham Young University*; E. Minot,* Cornell University*; D. Tanenbaum,* Pomona College*; P. McEuen,* Cornell University*; R.C. Davis,* Brigham Young University

Nanotubes were grown over a lithographically defined set of trenches, 60 nm deep and 300 nm wide on a pitch of 500 nm. After finding a nanotube that crossed three or more trenches, we used an atomic force microscope (AFM) to measure the amount of force required to make a single-walled carbon nanotube slip along the silicon dioxide trench tops. This measurement was made by pushing down on the tube with the AFM probe until slip was observed in the force-distance curve. The amount of slack in the slipped tube was also measured by looking at neighboring trenches, giving a force per unit length result.

3:20pm **NS-WeA5 Structural, Electronic and Frictional Properties of Gold Nanoclusters in Decane under Constrained Geometries***, **S.H. Kim**, F. Ogletree,* Lawrence Berkeley National Laboratory, University of California, Berkeley*; S. Hwang, Y.-S. Shon,* Western Kentucky University*; M. Salmeron,* Lawrence Berkeley National Laboratory, University of California, Berkeley

We investigated the behavior of gold nanoclusters suspended in decane (C@sub 10@H@sub 22@) when confined in narrow gaps of a few nanometers. The gaps are made by two parallel and atomically smooth mica surfaces in the Surface Force Apparatus (SFA). The diameter of the nanoclusters ranges from 1.8 to 3.2 nm. They are capped with alkanethiolate ligands of different lengths (C@sub 6@S or C@sub 15@S) to prevent metallic contact. Layering transitions of at least 3 layers are observed, indicating that the nanoclusters form ordered layers in the confined geometry. The mechanical and tribological properties (compressibility, shear resistance), and the dielectric properties of these clusters show remarkable variations with size, ligand length and confining pressure.

3:40pm **NS-WeA6 Nanoporous Au: Surface Characterization and Mechanical Properties***, **J. Biener**, A.M. Hodge, K.J.J. Wu, L.L. Hsiung,* Lawrence Livermore National Laboratory

Nanoporous Au prepared by electrochemically-driven dealloying of Ag-Au alloys has attracted considerable interest due to potential sensor and actuator applications. These materials exhibit an open sponge-like structure of interconnecting ligaments with an unimodal pore size distribution on the nanometer length scale. Due to a high surface-area to volume ratio, the properties of nanoporous materials should be influenced strongly by their surface properties. However, little is known about the surface chemistry of these materials. Here we will present our recent results regarding surface characterization and nanomechanical properties of nanoporous Au with a nominal relative density of ~30%. Time-of flight secondary ion mass spectroscopy (TOF-SIMS) was employed to obtain high-resolution, mass-resolved images of as-prepared Au foam surfaces. Our studies reveal the presence of adsorbed species such as chloride and nitrate from the dealloying process. It is well known from single crystal experiments that these species strongly interact with the Au surface, e.g. chlorine lifts the herringbone reconstruction on Au(111). This example demonstrates the necessity of surface science studies to better understand the properties of these nanoscale materials. The mechanical properties such as modulus and hardness of nanoporous gold were studied by nanoindentation combined with scanning electron microscope (SEM) characterization. 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.

4:00pm **NS-WeA7 Nanotribological Properties of Ultrananocrystalline Diamond***, **D.S. Grierson**, A.V. Sumant,* University of Wisconsin-Madison*; J.E. Gerbi,* Argonne National Laboratory*; J.P. Birrell,* Argonne National Laboratory, U.S.*; J.A. Carlisle, O.H. Auciello,* Argonne National Laboratory*; R.W. Carpick,* University of Wisconsin-Madison

The development of micro- and nano-scale devices with moving parts continues to progress rapidly, but the issue of tribological failure remains critical. The high surface-to-volume ratio at small scales requires that nano-scale adhesion and friction be characterized and reduced. Silicon, the main material currently used in micro- and nanodevices, suffers from poor tribological properties. Ultrananocrystalline diamond (UNCD) is a thin film material that may be far superior tribologically. We present the first measurements of nano-scale adhesion and friction of the tribologically relevant underside of UNCD. This surface is far less adhesive than a silicon reference sample. Furthermore, UNCD can be processed to render it chemically identical to single crystal diamond, minimizing the work of adhesion to the van der Waals limit and strongly reducing friction as well. Our methodology is not only applicable to diamond-based devices but could very well be extended to any thin film material.

4:20pm **NS-WeA8 Gas Phase Lubrication of MEMS***, **S.A. Smallwood**,* Universal Technology Corporation*; K.C. Eapen,* University of Dayton Research Institute*; J.S. Zabinski,* Air Force Research Laboratory (AFRL/MLBT)

A number of different MEMS systems have been designed, fabricated and a few have been marketed. Most commercial MEMS designs are void of parts that simultaneously move and undergo contact due to the problems of stiction, friction and wear. Candidate solutions to tribological problems include monolayers and self-lubricating hard materials. The problem with thin film lubricants is that the coating is fairly quickly worn away. Even though hard coatings such as diamond like carbon (DLC) are expected to have a longer life, improvements in durability are still required. A combination of bound and mobile phase lubricants has been used to extend life through flow of the mobile phase. This provides a protective bound coating and a fluid mobile constituent that offers replenishment. Another replenishment scheme is gas phase lubrication, which offers a way to continuously provide a protective coating by constantly replenishing the contact region. Gas phase lubrication results for MEMS are discussed in this talk. Accelerated screening tests have been performed in vacuum with a pin on disk tribometer tester using a range of Hertzian mean normal stress from 180 to 390 MPa. The tribometer includes a 0.25 inch dia. silicon nitride ball against a polysilicon sample. Protective gases were leaked into the vacuum system during friction tests. These gases include low boiling organic compounds with different functional groups. Surface tribochemistry in the wear track and wear debris were examined using x-ray photoelectron spectroscopy (XPS), microRaman spectroscopy, IR spectroscopy and scanning electron microscopy (SEM). In addition, performance tests were run on operational electrostatic MEMS motors. Surface chemical analyses on screening tests and operational devices are used to provide information on friction and wear mechanisms.

4:40pm **NS-WeA9 Novel Tribological Properties of Quasicrystals in Ultra-High Vacuum**, ***J.Y. Park***, *D.F. Ogletree, M. Salmeron,* Lawrence Berkeley National Laboratory; *C.J. Jenks, P.A. Thiel,* Ames Laboratory, Iowa State University

The structural and tribological properties of the interface between decagonal Al-Ni-Co quasicrystals and conductive TiN-coated cantilevers have been investigated. This was accomplished using a combined atomic force and scanning tunneling microscopy apparatus in ultrahigh vacuum. Atomically resolved STM images of the 2-fold Al-Ni-Co surface were obtained showing a clear periodicity along 10-fold direction, and a quasi-periodicity (following Fibonacci sequences) along the 2-fold direction. To decrease the high adhesion between the atomically clean quasicrystal surface and the metallic AFM tip (with has high adhesion force as large as 1000 nN), the tip or the surface were passivated by hydrocarbon molecules (ethylene and alkylthiol), which made possible the formation of stable contacts. This allowed us to observe an elastic to plastic transition occurring at a threshold load. With alkylthiol passivated tips the friction properties of the highly anisotropic 2-fold surface could be studied. We found a strong dependence of the friction force on the scanning direction, with low friction occurring along the aperiodic direction and high friction in the periodic direction. This result will be discussed in light of friction models of the interface based on existence or not of commensurability between the two contacting surfaces.

5:00pm **NS-WeA10 Quartz Crystal Microbalance Studies of the Friction of Rotating vs. Rigid C60**, ***T. Coffey***, Appalachian State University; *J. Krim,* North Carolina State University

Since C@sub 60@ was first discovered, it has intrigued tribologists. Due to its weak van der Waals interaction with most materials, its round shape, and its rapid rotation within its lattice position, many had hopes that C@sub 60@ would make an excellent lubricant, and drew analogies to nano-scale ball bearings. Although most experiments have shown that C@sub 60@ is a comparatively poor lubricant, the question of how the rotation of C@sub 60@ affects friction is still an interesting one. We have designed a Quartz Crystal Microbalance (QCM) experiment in ultra-high vacuum to determine how the rotation of C@sub 60@affects slip time (friction). In this experiment, we compare the slippage of methanol at room temperature on one monolayer of stationary C@sub 60@ or slowly rotating (~1 Hz) C@sub 60@ and two layers of quickly rotating (~10@super 9@ Hz) C@sub 60@. We found that the stationary monolayer of C@sub 60@ had longer slip times, or lower friction, than the quickly rotating C@sub 60@, defying the ball-bearing analogy.

Plasma Science and Technology
Room 213A - Session PS-WeA

Plasma Diagnostics

Moderator: W.M.M. Kessels, Eindhoven University of Technology, The Netherlands

2:00pm **PS-WeA1 Excitation Mechanisms in Low Pressure Capacitively Coupled Discharges**, ***G.F. Franz***, University of Applied Sciences, Germany; *M.K. Klick,* Advanced Semiconductor Instruments, Germany

The dominating excitation mechanisms in capacitively coupled discharges are ohmic heating (mainly to electrons in the bulk, and, at high powers, also to the ions in the sheath) and stochastic heating (thermalization of the electric energy of the sheath). The latter process will gradually enhance its importance when the discharge pressure is reduced below a threshold value of about 100 mTorr. That means that the electron energy distribution function (EEDF) in this regime will be governed by stochastic heating. This is also the pressure range in which reactive ion etching takes place. Measurements with self-excited electron resonance spectroscopy (SEERS) in various plasmas reveal that stochastic heating will strongly depend on the nature of the gas (atomic or molecular, electronegative or electropositive). Since ohmic heating scales with discharge pressure whereas stochastic heating is nearly pressure independent, both the heating mechanisms can be separated. New results are presented which have simultaneously measured with VI- and Langmuir probes as well as with optical emission spectroscopy (OES) with traces of rare gases and are eventually compared with models created by Lieberman, Godyak, and Klick.

2:20pm **PS-WeA2 Influence of Frequency on the Characteristics of UHF Capacitively Coupled Plasmas in a 300 mm Chamber**, ***G.A. Hebner***, *E.V. Barnat, P.A. Miller,* Sandia National Laboratories; *A.M. Paterson, J.P. Holland, T. Lill,* Applied Materials, Inc.

We have investigated the characteristics of UHF capacitively coupled plasmas produced in a modified Applied Materials chamber. The chamber had a 14-inch diameter upper electrode (source) that was driven at 10 to 160 MHz and a 300 mm diameter electrostatic chuck with a ceramic process kit that was driven at 13.56 MHz (bias). Diagnostics employed include a microwave interferometer to measure the line-integrated electron density, a hairpin microwave resonator to measure the spatially resolved electron density, absorption spectroscopy to determine the argon metastable temperature and density, laser induced fluorescence (LIF) to determine the spatial distribution of the excited species, and spatially resolved optical emission. We found that for constant source rf power, the electron density increased with rf frequency. The argon 1s5 metastable temperature was slightly above room temperature (300 â?" 400K), significantly cooler than our previous measurements in inductively coupled plasmas. The metastable density was not a strong function of source frequency or rf power. The metastable spatial distribution was always peaked in the center of the chamber and had a weak dependence on frequency. Scaling of the plasma parameters with frequency, power and pressure, and implications to energy deposition models will be discussed. This work was supported by Applied Materials and Sandia National Laboratories, a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company for the United States Department of Energyâ?Ts National Nuclear Security Administration under contract DE-AC04-94AL85000.

2:40pm **PS-WeA3 Monitoring Electron Density of Processing Plasmas Using a Transmission-line Type Microwave Sensor**, *C.H. Hseih,* National Tsing Hua University, Taiwan; ***K.C. Leou,*** National Tsing Hua University, Taiwan, ROC; *C. Lin,* National Tsing Hua University, Taiwan

The purpose of this study@footnote 1@, was to develop an electron density sensor for applications in process real-time feedback control of plasma based semiconductor fabrication tools, such plasma etchers or PECVDs. The sensor was a dielectric waveguide based transmission-line where microwave propagates at a phase velocity determined by the structure and the plasma density (electron density) surrounding the structure. Thus the variation of plasma density can be estimated from the phase shift of the transmitted microwave from one to the other end of the transmission-line. For the proof-of-principle study, a coaxial type transmission-line was adopted with a Teflon outer dielectric and a copper inner conductor operated at a freqeuncy of 2-3 GHz. Analytical analysis of dispersion characteristics of the transmission line structure was carried and the resulting propagation constants were in good agreement with results from calculation using a commercial high frequency structure simulation code (HFSS by ANSOFT). Experimental demonstration have been performed with an inductively-coupled plasma. The sensor was mounted on the inner wall of plasma chamber with a coaxial line length of 8 cm and a distance of 5 cm between input and output ports. Measurement results show that the dependence of electron density of plasma source RF power predicted by the sensor agrees well with the Langmuir probe measurements. Compared to conventional microwave interferometers where line-averaged plasma density is measured, the trainsmission-line type microwave sensor will be less susceptive to the interference caused by multi-passes reflection/refraction effect resulting from nonuniformity of plasma density profiles. Therefore, it provides a measurement of higher sensitivity and wider dynamic range. @FootnoteText@ Work supported by the grant from the National Science Concil of R.O.C. under contract #92-2218-E-007-018.

3:00pm **PS-WeA4 Real-time Monitoring of Charge Accumulated during SiO@sub 2@ Etching using Pulse-Time-Modulated-Plasma***, **Y. Suzuki**, T. Shimmura, S. Samukawa,* Tohoku University, Japan

High aspect ratio SiO@sub 2@ contact hole etching is crucial for ULSI device fabrication. However, serious problems, such as charge-build-up damage, etching stops and microloading effect, mainly caused by charge accumulated in contact holes are not clearly solved. Therefore, it is very important to measure the amount of charges and to control such charge accumulated. In this paper, we monitored the amount of charge accumulated in real-time during the continuous wave (CW) and pulse-time-modulated (TM) plasma etching for a number of contact holes by using on-wafer monitoring device. This sensor consists of Poly-Si (300nm) / SiO@sub 2@ (1.7 µmm) / Poly-Si (300nm) layered structure on Si substrate. The diameter of contact holes was 300nm, the numbers of that were 6,400,000 and aspect ratio was 5.7. The potential differences between the top and bottom Poly-Si electrodes were measured during plasma discharge. In the case of TM plasma, the potential differences drastically reduced, compared to the CW plasma. The time-resolved measurement showed the potential differences were increased during a few tens of micro-seconds of pulse-on-time and was reduced during a few tens of micro-seconds of pulse-off-time. As the charge accumulated were saturated at the time constant of milli-seconds on the substrate surface, theresult suggests that a few tens micro-seconds TM plasma can drastically reduce the charge accumulated on the surface. The proposed on-wafer monitoring sensor can realize the real-time measurement of charge accumulated during the plasma etching processes.

3:20pm **PS-WeA5 The Use of the Radio Frequency Matching Network As a Diagnostic for Plasma Processing Chambers***, **J. Caughman**, G.L. Bell,* Oak Ridge National Laboratory*; V. Resta,* Hewlett-Packard

Radio frequency (RF) power is commonly used in the plasma processing of semiconductors. As part of the RF system, many of the plasma processing chambers use RF matching networks with two variable tuning elements to transform the impedance at the chamber interface to be 50 ohms at the input of the matching network. The matching network is a highly tuned circuit, and the positions of the tuning elements are directly related to the RF impedance of the chamber. Thus, the positions of the tuning elements can be used as a diagnostic to determine processing sensitive parameters. Matching networks have been characterized to relate tuning element positions to the RF impedance and the power efficiency of the network. After characterization, the impedance and efficiency can be determined as a function of processing parameters simply by measuring the tuning element positions during processing. The technique has been demonstrated on both inductively coupled plasmas (ICP) and capacitively coupled plasmas (CCP). It has been found that the impedance is sensitive to changes in power, pressure, gas composition, and wall conditions. For example, an increase in ICP source power will cause an increase in the plasma density, which can be seen as an increase in the real part of the source impedance and a decrease in the real part of the bias impedance. The technique has been used on several different chambers and has been demonstrated to be helpful in terms of troubleshooting and chamber matching. Details of the characterization technique and the sensitivity of the impedance to processing conditions will be presented.

3:40pm **PS-WeA6 Measurements and Consequences of Non-Uniform RF Plasma Potential due to Surface Asymmetry in Large Area RF Capacitive Reactors***, **L. Sansonnens**, L. Derendinger, C. Hollenstein, A.A. Howling, H. Schmidt,* Ecole Polytechnique Fédérale de Lausanne, Switzerland*; J.P.M. Schmitt, E. Sakanaka,* UNAXIS-France SA, France

In small area capacitive reactors, the RF and DC plasma potential can be assumed to be uniform over the reactor area, and asymmetry between the grounded and powered electrodes leads to the well-known area law for determining the uniform DC and RF voltage amplitude across both plasma sheaths. In large area reactors, however, the RF plasma potential can vary over a long range across the reactor area due to the finite plasma conductivity. A local asymmetry of electrode area due, for example, to the lateral grounded walls for plasma confinement, causes a local RF plasma potential perturbation which propagates along the resistive plasma between capacitive sheaths. This propagation can be described by a telegraph equation for which a typical damping length can be determined. In this way, for a non-symmetric reactor wider than the damping length, the RF sheath voltage amplitudes which are unequal close to the reactor edges tend to be the same in the centre as for a symmetric reactor. A predicted consequence of this non-uniform RF plasma potential is the presence of non-ambipolar current circulating through the plasma and along conducting electrodes. In this work, we present measurements of the RF plasma potential and DC net current distribution over the grounded electrode of a large area reactor (57 x 47 cm@super 2@) using an array of surface probes, for various reactor geometry configurations. These experimental results are compared with a two-dimensional solution of the telegraph propagation model. Finally, we present some effects of the non-uniform RF plasma potential such as non-uniform power dissipation in the plasma which have important consequences for plasma processing.

4:00pm **PS-WeA7 Radiofrequency Discharge and Sheath Structure Around Dissimilar Surfaces***, **E.V. Barnat**, G.A. Hebner,* Sandia National Laboratories

Discontinuities present on a surface introduce perturbations to both the field and excitation around the discontinuity. Spatially resolved electric fields in an argon sheath near the discontinuous surfaces were measured using laser-induced fluorescence-dip spectroscopy (LIF-dip) while excitation is measured by LIF, optical emission and a Langmuir probe. Spatial maps of the electric field and excitation were obtained in the regions near these discontinuities as functions of power and pressure of the discharge. These measurements demonstrate the degree and extent of perturbation introduced into the plasma. Surface discontinuities investigated included metal-dielectric, metal-metal and metal-step junctions. 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 Energyâ?Ts National Nuclear Security Administration under contract DE-AC04-94AL85000.

4:20pm **PS-WeA8 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.

4:40pm **PS-WeA9 Investigation of Correlation between Etching Profiles and Neutral Density in Cl@sub 2@/O@SUB 2@ Plasmas***, **M. Mori**,* Hitachi Ltd., Japan*; G. Cunge, M. Kogelschatz,* CNRS/LSP, France*; L. Vallier,* CNRS/LTM, France

Cl@sub 2@/O@sub 2@ plasmas are basically used in Shallow Trench Isolation (STI) etching of ULSI device fabrication. In STI etching, precise taper angle control is one of the issues for good coverage without stress damage to Si substrate at following deposition process. The taper angle is determined by the sidewall passivation layer during etching. Hence etching by-products (SiCl@sub x@) are thought to play an important role in taper angle control, because they are believed to be the precursors to the deposition of sidewall passivation layers. In this study, we have investigated the correlation between SiCl@sub x@ density and etching profiles in Cl@sub 2@/O@sub 2@ plasmas. The SiCl@sub x@(X=0-2) absolute densities are measured by UV broad band absorption spectroscopy. The thickness of the sidewall passivation layer is measured by comparing the etched profiles before and after removal of the passivation layer. The SEM results firstly confirm that good correlation between the taper angles and the thickness of the passivation layer on feature sidewalls over a wide range of plasma operating conditions (pressure, source power, O@SUB 2@ flow rate and total gas flow rate). By contrast, there is no correlation between the thickness of sidewall passivation layers and the SiCl@sub x@ densities in the plasma. For example, the passivation layer thickness increases rapidly while the SiCl@sub x@ density decrease with increasing O@SUB 2@ gas flow. Indeed, our data suggests that the growth rate of sidewall passivation layers is limited only by the O density in the plasma, which thus controls the etching profile. By roughly calculating O atom density as a function of electron temperature and density, we are then able to explain the trend of passivation layer thickness with pressure and source power. The role of O is to oxidize SiCl@sub x@ species chemisorbed on the surfaces exposed to the plasma, which, without oxidation are etched back into the plasma by Cl atoms.

5:00pm **PS-WeA10 2D-Imaging Measurements of Sputtered Atom Velocities in dc Magnetron Discharges by Doppler-Shifted LIF*, K. Sasaki,*** Nagoya University, Japan*; K. Shibagaki,* Suzuka National College of Technology, Japan*; N. Nafarizal, H. Toyoda, T. Kato, S. Iwata, S. Tsunashima, H. Sugai,* Nagoya University, Japan

In the deposition of multilayer magnetic thin films such as Co/Pt and Fe/Pt using magnetron sputtering discharges, a key issue is how to obtain very flat interfaces between the multilayers. Bombardment of energetic ions and neutrals during deposition may roughen the interface. Understanding on energies of particles supplied to the substrate is helpful to optimize the apparatus for the deposition of multilayer magnetic films. In the present work, we measured the spatial distribution of velocity distribution of Fe atoms in a conventional dc magnetron discharges. We employed laser-induced fluorescence imaging spectroscopy. By recording pictures of laser-induced fluorescence at various wavelengths of a tunable optical parametric oscillator, we obtained many Doppler spectra that represent the velocity distributions of Fe atoms in a r-z plane of the cylindrically symmetric magnetron discharge. In a low-pressure discharge at 3 mTorr, Fe atoms near the target had broad velocity distribution, and they contained energetic component with velocity faster than 10 km/s (29 eV). At a distance of 60 mm from the target, Fe atoms had a thermalized distribution having two temperatures. By integrating the velocity distribution, we obtained two-dimensional maps of the mean velocity of Fe atoms. In a low gas pressure of 3 mTorr, Fe atoms had a mean velocity of 3.6 km/s in the region adjacent to the target surface. In a gas pressure of 20 mTorr, the mean velocity of Fe adjacent to the target was slower than 1 km/s. This work was supported by the 21st Century COE Program by the Ministry of Education, Culture, Sports, Science and Technology of Japan.

Semiconductors
Room 304C - Session SC-WeA
Narrow Gap Semiconductors

Moderator: J. Zinck, Hughes Research Laboratories

2:00pm **SC-WeA1 Growth and Properties of Dilute Nitride Semiconductors with a Bismuth Surfactant*, T. Tiedje,*** *D,A, Beaton, S. Tixier, M.B. Whitwick, E.C. Young, N.R. Zangenberg,* University of British Columbia, Canada*; S. Francoeur,* National Renewable Energy Laboratory **INVITED**

The dilute nitride semiconductor In@suby@Ga@sub1-y@As@sub1-x@N@subx@ is a promising new III-V alloy for solar cells and lasers in which low concentrations of N cause an anomalous reduction in the bandgap. N alloying degrades the electronic properties, possibly through formation of localized N cluster states. We show that the electronic properties of GaAs@sub1-x@N@subx@ can be improved with the use of a Bi surfactant during plasma assisted MBE growth. The effect of modifying the active nitrogen species (ratio of atoms to excited state molecules) in plasma-assisted MBE growth has also been explored. The Bi surfactant reduces the surface roughness by a factor of ten and produces step flow growth at temperatures as low as 460°C. The surfactant also improves the room temperature photoluminescence (PL) efficiency in as-grown and annealed samples, and reduces the density of shallow gap states, as determined from the shape of the PL spectra. The N incorporation increases with the Bi coverage by up to 50% when the surface is saturated with Bi. In-situ mass spectroscopy experiments show that NAs (but not NBi) is present in the gas phase, during growth and that the partial pressure of NAs increases slightly with Bi flux, suggesting that the Bi surface layer enhances the reaction of active nitrogen with GaAs. The Bi covers the surface but does not incorporate (@450°C. If the As:Ga flux ratio is reduced to approximately 1:1, Bi will incorporate at low substrate temperatures (380°C). The dilute Bi alloys show room temperature photoluminescence @footnote1@ and similar to the dilute nitrides the bandgap has an anomalously large concentration dependence. @FootnoteText@ @footnote1@S. Tixier et al, Appl. Phys. Lett. 82, 2245 (2003).

2:40pm **SC-WeA3 Nitrogen Incorporation in GaAsN Films and GaAsN/GaAs Superlattices*, H.A. McKay,*** *M. Reason, X. Weng, N. Rudawski, W. Ye, V. Rotberg, R.S. Goldman,* University of Michigan

GaAsN and InGaAsN alloys with a few percent N have potential applications in infrared laser diodes, high efficiency solar cells, and other electronic devices. However, as-grown materials often exhibit poor photoluminescence efficiencies and lower than expected carrier concentrations and mobilities. A few studies have suggested that control of N incorporation via ex-situ annealing or superlattice (SL) growth may lead to improved optical and electronic properties. In this work, we are exploring in-situ approaches to controlling N incorporation during the growth of GaAsN films and GaAsN/GaAs SLs. In the case of GaAsN films, we have investigated N incorporation in GaAsN films grown by solid-source molecular beam epitaxy (MBE) using a 10% N@sub 2@/90%Ar or pure N@sub 2@ RF plasma source, with As@sub 2@ or As@sub 4@, and a variety of growth temperatures, Si-doping, and V/III ratios. Nuclear Reaction Analysis and Rutherford Backscattering Spectrometry in channeling and non-channeling conditions reveal significant composition-dependent non-substitutional incorporation of N, presumably as N-N or N-As split interstitials. We find that non-substitutional N incorporation is minimized for films grown at 400@super o@C with pure N@sub 2@, apparently independent of As species, Si-doping, and V/III ratio. In the case of GaAsN/GaAs SLs, we have developed an in-situ approach to prevent incorporation of N into the GaAs barriers of the superlattice, using an independently-pumped plasma source chamber, separated from the MBE via a gate valve. High-resolution x-ray diffraction studies reveal significant improvements in the interface quality for superlattices prepared with the active N flux controlled via the gate valve in comparison with a conventional shuttering approach. The effects of N incorporation on the electrical and optical properties of GaAsN films and GaAsN/GaAs SLs will also be presented. @FootnoteText@ This work is supported by DOE, AFOSR-MURI, NSF-NER, NASA-Lewis, and TRW.

3:00pm **SC-WeA4 Optical Properties of GaAs@sub 1-x@N@sub x@: A Tight Binding and Variable Angle Spectroscopic Ellipsometry Study*, S. Turcotte,*** *S. Larouche, J.-N. Beaudry, N. Shtinkov, L. Martinu, R.A. Masut,* École Polytechnique de Montréal, Canada*; R. Leonelli,* Université de Montréal, Canada*; P. Desjardins,* École Polytechnique de Montréal, Canada

We have carried out a series of tight-binding (TB) calculations and variable-angle spectroscopic ellipsometry (VASE) measurements in order to investigate the excited states above the band gap of GaAs@sub 1-x@N@sub x@ layers on GaAs(001). The calculations are carried out using an empirical TB model in the sp@super 3@d@super 5@s*s@sub N@ parameterization, which provides a band-anticrossing description of the GaAs@sub 1-x@N@sub x@ band structure over the entire Brillouin zone for energies up to 5 eV above the valence band maximum. A series of fully-coherent GaAs@sub 1-x@N@sub x@ layers with x up to 0.012 were grown on GaAs(001) by organometallic vapor phase epitaxy using trimethylgallium, tertiarybutylarsine, and dimethylhydrazine precursors. The GaAsN dielectric function was reliably determined from 0.76 to 4.4 eV through point by point fitting of the experimental data with a model which also takes into account the GaAs substrate and the oxide overlayer. In addition to the band edge transition E@sub -@, the L point related optical transition E@sub 1@ and their split-off replica, we also observe, for the first time in room temperature VASE measurements, the E@sub +@ level signature which appears as a well defined critical point contribution to the dielectric function. The comparison between experimental data and TB calculations provides information on the specific contributions of the different Brillouin zone points to the GaAsN dispersion curves.

3:20pm **SC-WeA5 Growth Modes of InN on Sapphire (0001) with GaN Buffer Layers***, S.R. Leone,* University of California*;* ***B. Liu,*** *D.X. Chen,* Lawrence Berkeley National Laboratory*; T. Kitajima,* National Defense Academy of Japan

InN is an important group-III nitride semiconductor. Use of InN can extend the working wavelength of the nitride-based optoelectronic devices from ultraviolet to infrared. However, heteroepitaxy of InN has encountered difficulties due to the thermal instability of InN and the large lattice mismatches between InN and the commonly used substrates (e.g., sapphire). During growth, the high equilibrium pressure of nitrogen requires a high V/III flux ratio to suppress InN decomposition, which often results in undesired three-dimensional (3D) rough surfaces. In this work, using atomic force microscopy (AFM) and scanning tunneling microscopy (STM), we study the growth modes and the surface morphologies of InN grown by plasma-assisted molecular beam epitaxy on sapphire (0001) substrates with intermediate GaN buffer layers. With smooth GaN buffer layers, 3D InN islands are observed to have mesa-like shapes with atomically flat tops. However, prolonged growth in this mode does not produce continuous two-dimensional (2D) InN films by coalescence of InN islands. With 3D rough GaN buffer layers, continuous 2D InN films are obtained showing the characteristics of step-flow growth. STM imaging reveals the defect-mediated surface morphology of the 2D InN films, including surface termination of screw (or mixed) dislocations and a high density of shallow surface pits with depths of about 0.1 nm. The mechanisms of the different growth modes and surface defect formation are also discussed.

3:40pm **SC-WeA6 Energy Gap and Stokes-like Shift in Cubic In@sub x@ Ga@sub 1-x@N Epitaxial Layers**, *DG Pacheco-Salazar, J.R.L. Fernandez,* University of Sao Paulo, Brazil*; **J. Soares**,* University of Illinois at Urbana Champaign*; J.R. Leite,* University of Sao Paulo, Brazil*; F. Cerdeira, E.A. Meneses,* University of Campinas, Brazil*; S.F. Li, O. Husberg, D.J. As, K. Lischka,* University of Paderborn, Germany

Group-III nitrides have been intensively investigated due to their recent applications in optoelectronic and electronic devices. The light emission mechanism of efficient blue-green-ultraviolet LED and laser diodes based on these materials is still object of investigation, and several works have been carried out recently on the optical properties of the In@sub x@Ga@sub 1-x@N alloy, the active medium in these optoelectronic devices. In the present work photoluminescence (PL), photoluminescence excitation (PLE) and Cathodoluminescence (CL) are used to investigate emission and absorption mechanisms in cubic 100 nm thick In@sub x@Ga@sub 1-x@N epitaxial layers grown on thick GaN/GaAs(001) buffer layers by MBE. High resolution x-ray diffraction (HRXRD) revealed that the InGaN layers were pseudomorphic with the GaN buffer. The In fraction x was calculated from the strained lattice constants obtained from the HRXRD reciprocal space maps. Reflectivity was used to measure the thickness of our films. PL and PLE spectra were recorded at 7 K and 300 K. CL spectra were performed at room temperature. The main features observed in the PL spectra are the characteristic emission from the band edge region of c-GaN and a lower energy peak which we ascribe to the InGaN layer. From the PLE spectra, we have determinated the alloy energy gap as a function of the In content. Comparing results from PL and PLE we observe a large Stokes-like shift for all samples. Another absorption band at lower energy than that of the alloy energy gap is observed on some of the PLE spectra. We tentatively ascribe this band to an absorption mechanism taking place in In-rich regions in the InGaN alloy. These findings are supported by a multi-peak structure obtained by PL and depth-resolved CL. In depht-resolved CL, the relative intensity of the peaks changes with increasing excitation depth, indicating a second InGaN fase close to the GaN/InGaN interface.

4:00pm **SC-WeA7 InAs-based Heterojunction Bipolar Transistors***, **P.W. Deelman**, P.D. Brewer, D.H. Chow, K.R. Elliott, T. Hussain, R.D. Rajavel, S.S. Thomas, III,* HRL Laboratories **INVITED**

We have demonstrated the first InAs-based heterojunction bipolar transistors (HBTs) with f@sub T@ and f@sub max@ simultaneously exceeding 100GHz. Our best small-area (0.4 × 3.0 @micron@@super 2@) HBTs feature an f@sub T@ of 215GHz, a V@sub be@ of 0.35V, and a @beta@ of 60. Using similar devices, we have successfully fabricated the world's first InAs-based integrated circuit - - - a divide-by-sixteen circuit operating at 27GHz. The divider consists of 62 transistors fabricated on a 3" wafer. The promise that HBTs nearly-lattice-matched to InAs potentially operate at higher frequencies and with lower power-delay products than current technologies motivated this work. Nevertheless, we have had to overcome several materials-related obstacles in order to achieve these results. For example, insulating substrates for the 6.1@Ao@ family of materials do not exist, and the nature of the band alignments in these materials dictate that at least one, if not all, the layers in the structure be strained. We employed two approaches to deal with the substrate issues. InAs transistors were grown by molecular beam epitaxy either on InP substrates using semi-insulating, strain-relaxed AlGaAsSb buffers or coherently on 3" InAs substrates. The latter approach required subsequent wafer bonding to sapphire carriers. Our baseline structures utilized either an InAsP or AlInAs emitter and an InAs base. For some devices, the emitter was graded to reduce strain energy. Current gain decreases for base doping levels above 1×10@super 19@ cm@super -3@; however, even with heavily Be-doped (~2 × 19 cm@super -3@) InAs bases, we obtain high @beta@ (>60). Numerical simulations provide an insight into the deleterious implications of Be diffusion, the degree of which can be manipulated through the MBE growth process. The work described in this talk was sponsored by DARPA/SPAWAR under contract number N66000-01-C-8033.

4:40pm **SC-WeA9 Lattice Constant Differences and Their Affect on the Surface Bonding of In@sub 2@O and Ga@sub 2@O on GaAs and InAs***, **M.J. Hale**, D.L. Winn, J.Z. Sexton, M. Passlack, A.C. Kummel,* University of California, San Diego

The atomic bonding structures formed upon deposition of In@sub 2@O on GaAs(001)-c(2x8)/(2x4) and InAs(001)-c(2x8)/(2x4) were identified through scanning tunneling microscopy and density functional theory calculations. These results were compared to the surface bonding structure of Ga@sub 2@O deposited on GaAs(001)-c(2x8)/(2x4). It was found that In@sub 2@O forms three distinct bonding configurations on the GaAs(001)-c(2x8)/(2x4) surface: two different configurations which span the trough, and one which inserts into row arsenic dimer pairs. When In@sub 2@--O was deposited on the InAs(001)-c(2x8)/(2x4) surface only the row As dimer pair site was observed. This effect is attributed to the In@sub 2@O molecule being large enough to span the 8.0Å trough of the GaAs(001)-c(2x8)/(2x4) surface, but too small to span the 8.6Å trough of InAs(001)-c(2x8)/(2x4). The In@sub 2@O bonding site on InAs(001)-c(2x8)/(2x4) is analogous to the binding site for Ga@sub 2@O on GaAs(001)-c(2x8)/(2x4), where Ga@sub 2@O is found to bond only in row arsenic dimer pairs. The change in lattice constant between InAs and GaAs is also found to have an affect on Fermi level pinning. Through experiments and DFT calculations, we have shown that In@sub 2@O pins GaAs whereas Ga@sub 2@O does not. DFT calculations also show that we should not expect In@sub 2@O to pin InAs. Our results show that a modest change in lattice constant can dramatically alter the adsorbate bonding and electronic structure via a change in site selectivity.

5:00pm **SC-WeA10 An Atomic Understanding of the Sub-Monolayer Interface formed Upon the Deposition of SiO on GaAs(001)-c(2x8)/(2x4)}***, **D.L. Winn**, M.J. Hale, J.Z. Sexton, M. Passlack, A.C. Kummel,* University of California, San Diego

Scientists have been trying to develop a GaAs-based MOSFET device in an effort to reduce standby power and gate leakage. To achieve this it is important to understand the chemistry at the oxide/semiconductor interface. The interface formed upon deposition of SiO on GaAs(001)-c(2x8)/(2x4) was studied using STM, scanning tunneling spectroscopy (STS) and DFT. STM images show that SiO molecules bond Si end down in three distinct locations: into row and trough As dimers and between row As dimers. It was also observed that when SiO bonds between row As dimers, the two adjacent dimers along the [1bar10] direction each contain an inserted SiO molecule forming a chain of three molecules (triple site). STS measurements show that ~5% of a monolayer of SiO pins the Fermi level at mid gap. This is consistent with SiO absorbates withdrawing charge from surface As atoms, causing charge on the As atoms to grossly deviate from the charge on bulk As atoms. Multiple SiO sites were simulated using DFT, the lowest energy structure however was not observed in STM. An energy versus chemical potential plot was used to explain and identify the most stable bonding structures in the coverage studied with STM. This plot showed that at low SiO coverages the most stable sites were single sites but at higher coverages the most stable sites shifted to sites involving three SiO molecules including the triple site. This work demonstrates the key role of coverage in determining the most stable bonding structure. For oxides on semiconductors there are usually multiple nearly degenerate bonding configurations and the coverage is the key variable in determining the relative chemical potentials

Surface Science
Room 213B - Session SS+OF-WeA

Contacts to Molecules and Molecular Films

Moderator: G.G. Malliaras, Cornell University

2:00pm **SS+OF-WeA1 Electron Transport at Interfaces and Junctions: Understanding Molecular Electronics***, X.-Y. Zhu,* University of Minnesota **INVITED**

Charge transport at or across molecule-electrode interfaces is central to the operation of a wide variety of molecule-based electroic devices. The critical charge transporting interfaces in most systems are buried interfaces which are not readily accessible to conventional structural or spectroscopic probes. For any given device, two critical questions are: (1) What is the structural and chemical nature of the molecules at the buried interface before or during operation? (2) How is the electrical conductance across an interface related to physical properties such as electronic energy level alignment and charge redistribution? This talk will attempt to address both questions from spectroscopic measurements and to demonstrate that such a spectroscopic view is of critical importance in achieving a quantitative understanding of moleular electronics.

2:40pm **SS+OF-WeA3 The Influence of Chemical Coupling Groups on the Electronic Structure of Conjugated Self-Assembled Molecular Monolayers***, **S.W. Robey,*** NIST*; C.D. Zangmeister,* NIST, US*; R.D. Van Zee,* NIST

The performance of conjugated molecular systems in electronic applications, either for organic light emitting diodes (OLED's) and field effect transistors, or in more speculative applications proposed for molecular electronics, depends critically on coupling at the molecule-electrode interface. Interactions at this interface determine the alignment of the contact Fermi level with the transport levels in the molecular system, which in turn controls charge injection into the molecular @pi@ levels. Using one-and two-photon photoemission to access occupied and unoccupied levels, we have examined the influence of the metal-molecule coupling chemistry on the Fermi level alignment and electronic structure in the prototypical "molecular wire", 4,4'-(ethynylphenyl)-1-benzenethiol system on Au. Photoelectron spectroscopies reveal an increase in the binding energies (relative to the Fermi level of Au) for the C @sigma@ and @pi@ derived valence levels and the C (1s) core level upon substitution of the isocyanide coupling for thiol. No spectral changes are observed, however, in the region of the molecular @pi@ levels important for transport. Optical absorption measurements also reveal no change in optical band gap. These results indicate that substitution of the isocyanide linking chemistry for thiol based chemistry leads to a large shift, by ~ .5 eV, of E@sub f@ away from the highest occupied level in the molecule, but little modification of the extended @pi@ molecular electronic structure. The interaction at the Au-thiol-OPE interface will be compared and contrasted with the Au-isocyanide-OPE interface in terms of bonding and charge transfer effects and contact made to RAIRS and transport data for related systems.

3:00pm **SS+OF-WeA4 Mechanical and Charge Transport Properties of Self Assembled Organic Monolayers***, **I. Ratera**, J.Y. Park, J. Chen, A. Liddle, D.F. Ogletree, M. Salmeron,* Lawrence Berkeley National Laboratory

We are interested in measuring and correlating electronic and mechanical properties of molecules. We will report our progress in the fabrication of insulating test substrates with embedded coplanar metallic nanoelectrodes. In this manner a monolayer of molecules can bridge two electrodes and be accessible to an AFM or STM tip. This approach may lead to a better understanding the nature of the molecule - electrode contact. The use of AFM with conducting tips provides the ability to vary the load on the nano-contact and also opens the way for exploring electron transfer as a function of molecular deformation. Initial results will be presented on the influence of mechanical stress on the structural and electrical properties of self-assembled alkylthiols on gold surfaces as a function of the chain length and tip pressure.

3:20pm **SS+OF-WeA5 Electronic Properties of Interfaces between Organic Semiconductors and Metals***, **M. Knupfer,*** Leibniz Institute for Solid State and Materials Research Dresden, Germany **INVITED**

The electronic properties and the energy level alignment of interfaces between organic semiconductors and metals have been studied using photoemission spectroscopy in the valence as well the core level region. Different contrubutions to the frequently observed interface dipoles are discussed. In particular, the role of a reduction of the metal workfunction in comparison to clean, uncovered surfaces and image charge screening will be addressed. Furthermore, there are several examples where a charge transfer is observed at the interface, in particular for technologically relevant cases, which is essential for the understanding of charge transport acroos the corresponding interface.

4:00pm **SS+OF-WeA7 Energy Level Alignment at Organic Interfaces: Interface Induced Gap States and Charge Neutrality Levels***, **T.U. Kampen,*** Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany

The energy level alignment at organic interfaces determines the efficiency of charge injection into organic films. Quite often the vacuum level alignment rule has been used to determine the energy level alignment at organic interfaces. Here, barrier heights can simply be calculated using the ionisation potentials or electron affinities of semiconductors materials and work functions of metals. For organic interfaces a conclusion has been reached that in general the vacuum levels do not align. At intimate, abrupt, and defect free interfaces of inorganic semiconductors interface induced gap states are the primary mechanism determining the energy level alignment. These interface states derive from the bulk states and their character changes across the band gap from more acceptor-like closer to the conduction band to predominantly donor-like nearer to the valence band. The branch point where the character changes has the significance of a charge neutrality level. This work shows that the concept of interface induced gap states may also be applied to organic interfaces. The charge neutrality levels of PTCDA, DiMe-PTCDI, and CuPc are found to be 1.96 eV, 1.93 eV, and 0.51 eV above the HOMO, respectively.

4:20pm **SS+OF-WeA8 Work Function and Charge Distribution XPS Study of Molecular Layers Self-Assembled on Gold***, H. Cohen, **S. Ray**, R. Naaman,* The Weizmann Institute of Science, Israel

Substrate-overlayer charge transfer frequently imposes considerable changes on the properties of self-assembled (SA) monolayers. The study of space charge distribution across molecular layers is targeted here, using XPS in a slightly modified setup, capable of in-situ work-function evaluation. Fine differentiation between chemical and electrical information across dipolar layers is demonstrated. Intra-molecular charge transfer is found to take place in part of the systems, giving rise to a directional flip of the dipole moment on the nanometer scale.

4:40pm **SS+OF-WeA9 Influence of Electrode Contamination on @alpha@-NPD/Au Hole-injection Barriers***, **A.S. Wan**, J.H. Hwang, A. Kahn,* Princeton University

Processing for OLEDs and other organic devices often involves exposure of surfaces and interfaces to nominally controlled atmosphere (e.g. N@sub 2@) or even ambient conditions. A model system for studying barriers built under such "practical" conditions, as opposed to barriers built on ultra-clean substrates prepared under ultra-high vacuum (UHV) conditions, is the interface between Au and @alpha@-NPD, a standard hole- transport material for OLEDs. In this work, we investigate the effect of ambient exposure of polycrystalline Au surfaces on the hole-injection barrier using ultraviolet photoemission spectroscopy (UPS) and I-V measurements. We compare @alpha@-NPD layers grown in UHV on: i. Au as-loaded, exposed to air; ii. Au cleaned by Ar@super +@ sputtering; iii. fresh Au deposited in UHV. Conventional wisdom is that the higher the work function of the contact metal, the lower the hole-injection barrier. However, our UPS studies unambiguously show that the injection barrier is 0.5-0.6 eV lower for Au exposed to air, which has a work function of 4.7-4.9 eV, than for clean Au (sputtered or UHV deposited), which has a work function of 5.3-5.4 eV. The vacuum level shift, or dipole barrier, (down from Au to organic) is 0.3 eV for the former and 1.3 eV for the latter. I-V measurements on Au/@alpha@-NPD/Au devices made on clean vs. "dirty" Au show several orders of magnitude increase in injection from "dirty" Au, entirely consistent with the changes in barriers measured in UPS. The large differences in dipole and injection barriers are attributed to the layer of contamination (consisting primarily of carbon) on the air- exposed Au, which lowers the work function of the metal and decouples the interface molecules from the Au atoms. Mechanisms based on disruption of interface bonding and/or metal-induced states will be discussed.

5:00pm **SS+OF-WeA10 Time-Evolution and Stability of Metal-Molecule Contacts***, G. Nagy, **A.V. Walker**,* Washington University in St. Louis

Understanding the nature of metal-molecule interactions is important for many technologies, including organic and molecular electronics. It has already been demonstrated using vapor-deposited metals on self-assembled monolayers (SAMs) that many interactions are possible, ranging from destruction of the SAM to organometallic formation to penetration through the SAM to the Au/S interface. We apply time-of-flight secondary ion mass spectrometry (TOF SIMS) experiments and density functional theory (DFT) calculations to investigate the time-evolution and the energetics of vapor-deposited metallic contacts. As model systems we are employing vapor-deposition of copper on alkanethiolate SAMs with -CH3, -OCH@sub 3@, -COOH, -OH and -COOCH@sub 3@ terminal groups. We observe at room temperature that vapor-deposited Cu on -COOH and -OCH@sub 3@ SAMs initially both penetrates to the Au/S interface and forms a weak complex with the terminal group. However, Cu at the vacuum interface is not stable in the long term and slowly penetrates through the monolayer. We demonstrate that the stability of metal-molecule contacts is dependent on a number of factors including the strengths of the metal-metal and the metal-molecule interactions and the rate of penetration through the monolayer, which itself is dependent on the diffusion of the SAM molecules on the Au substrate.

Surface Science
Room 210B - Session SS1-WeA
Metal Oxides and Clusters II: TiO@sub 2@ and Photocatalysis

Moderator: U. Diebold, Tulane University

2:00pm **SS1-WeA1 First-Principles Study of Intrinsic Defect Formation Energies in Tio@sub 2@*, J. He*,** *S.B. Sinnott,* University of Florida

First-principles calculations are used to study intrinsic defects in bulk rutile TiO@sub 2@ and on the TiO@sub 2@ (110) surface. The approach is density functional theory (DFT) using the generalized gradient approximation (GGA) combined with plane-wave ultrasoft pseudopotentials. In particular, the formation energies of isolated vacancies, interstitials, and substituents with different charges, representing localized or distributed charge states, are evaluated. The DFT calculation results are combined with thermodynamic data to calculate the defect formation energies. In particular, the influence of temperature and oxygen partial pressure on the oxygen chemical potential is taken into account. The calculations suggest that fully charged Ti interstitials are more stable than oxygen vacancies at most oxygen partial pressures. Contrary to expectations, our preliminary results also indicate that the formation energy behavior of O vacancies at the TiO@sub 2@(110) surface is similar to the formation energy behavior of O vacancies in bulk TiO@sub 2@. These results are helping us to understand defect formation and segregation in TiO@sub 2@.

2:20pm **SS1-WeA2 Comparison of Physisorption on MgO(100) and TiO@sub 2@(110) Surfaces*, Z. Dohnálek*,** *J. Kim, B.D. Kay,* Pacific Northwest National Laboratory

Characterization of oxide surfaces represents one of the current challenges in surface science. In this study we employ physisorption of weakly bound species such as N@sub 2@, O@sub 2@, CH@sub 4@, and Ar to determine the distribution of binding sites on the surfaces of MgO(100) and TiO@sub 2@(110). Cooling of the oxide surfaces to cryogenic temperatures (T < 30K) is critical for conduction such measurements. Both surfaces were extensively studied in the past and represent an ideal platform to correlate surface sites with binding energies of various adsorbates. On MgO(100) only a single temperature programmed desorption (TPD) monolayer feature is observed for all the adsorbates. This is a result of simplicity of unreconstructed MgO(100) surface with checkerboard like arrangement of Mg@super 2+@ and O@super 2-@ ions. TPD spectra observed on TiO@sub 2@(110) are in sharp contrast with those from MgO(100). In this case the surface structure composed of rows of Ti@super 4+@ ions and bridge-bonded oxygens leads to two distinct adsorption geometries. The coverage of the adsorbates in these two geometries is approximately the same and it in agreement with 1:1 ratio of Ti@super 4+@ and bridge-bonded O sites. Typical defects are also probed on both surfaces. On MgO(100) their coverages are determined to be on the order of 15%. Lower coordination of the defect sites results in increased adsorbate binding energies. The effect of oxygen vacancies on the physisorption on TiO@sub 2@(110) is currently being investigated. @FootnoteText@ Pacific Northwest National Laboratory is operated for the Department of Energy by Battelle under Contract DE-AC06-76RLO 1830.

2:40pm **SS1-WeA3 The Oxygen Chemistry on Rutile Titanium Dioxide*, E.K. Vestergaard*,** *E. Wahlström, R. Schaub, J. Matthiesen, F. Besenbacher,* Interdisciplinary Nanoscience Center, Denmark

The detailed understanding of the oxygen chemistry on titanium dioxide is an important issue for chemical and photo-chemical processes on this material. In particular, the detailed route for oxygen vacancy filling through oxygen exposure is important to understand the change of surface reactivity upon re-stoichiometrization. We present STM investigations resolving the atomic-scale details of adsorption, diffusion and reaction of oxygen molecules on the TiO@sub 2@(110) surface. By following the dynamical processes in real time with STM movies, we find that both the diffusion and the reaction between oxygen molecules have activation energies of approximately 0.35 eV and exhibit extremely low attempt frequencies of ~10@super 6@ s@super -1@. These findings are interpreted in a model where charge transfer processes from the TiO@sub 2@ conduction band to the adsorbed oxygen molecules govern the dynamics: Surface oxygen vacancies pin the chemical potential at 0.35 eV from the conduction band, in good agreement with the observed activation energy for diffusion of oxygen molecules.@footnote 1@ The same activation energy is also found for the dynamics of larger oxygen clusters containing three or more atoms. The interaction between such clusters and the bridging oxygen rows on the TiO@sub 2@(110) surface are found to be essential for the understanding of the ability of oxygen to heal the bridging oxygen vacancies. Finally, the presented STM results are discussed in the context of active support materials for Au catalysts. @FootnoteText@ @footnote 1@E. Wahlström et al., Science 303, 511 (2004).

3:00pm **SS1-WeA4 Charge Transfer-Induced Water Splitting on the Rutile TiO@sub 2@(110) Surface*, R. Schaub*,** *E. Wahlström, E.K. Vestergaard, J. Matthiesen, F. Besenbacher,* Interdisciplinary Nanoscience Center, Denmark

In direct contact with water, metal oxides are promising candidates in the search for renewable energy sources through direct photo-splitting of water as suggested by the seminal experiments of Fujishima and Honda@footnote 1@. TiO@sub 2@ is in particular one of the most utilized photo-chemically active systems for waste water treatment. For such photo-chemical processes, surface bound water as well as hydroxyls have been proposed to be the major species which are photo-activated to form hydroxyl radicals responsible for the photochemical activity. By means of scanning tunneling microscopy (STM) we have identified a number of different water-derived adsorbates on the TiO@sub 2@(110) surface, and the details of their formation were revealed from time-resolved STM movies. We find strong evidence that the diffusion of hydroxyls, as well as H@sub 2@O dissociation, is linked to the electronic properties of the substrate in the surface region, in a similar manner to our previous results reported for the interaction of O@sub 2@ molecules with TiO@sub 2@(110)@footnote 2@. Hence, charge transfer from the conduction band of the substrate to adsorbed molecules or reactants is identified as a key factor to understand their physical properties. In other words, chemical reactions can be promoted, not only by a localized "active" site (the traditional approach), but also by the more delocalized conduction band electrons. @FootnoteText@ @footnote 1@ A. Fujishima and K. Honda, Nature 238, 37 (1972).@footnote 2@ E. Wahlström et al., Science 303, 511 (2004).

3:20pm **SS1-WeA5 Photodecomposition of Acetone on TiO@sub 2@(110)*, M.A. Henderson*,** Pacific Northwest National Laboratory

Although acetone is commonly used to evaluate the performance of oxide photocatalysts, little is known about the mechanistic details of its photo-oxidation. This study provides insights into the photodecomposition of adsorbed acetone using the (110) face of rutile TiO@sub 2@ as a model photocatalyst. In the absence of UV light, acetone desorbs from the clean TiO@sub 2@(110) surface without decomposition, exhibiting strong coverage-dependence in its temperature programmed desorption (TPD) peak that shifts from 350 K to below 250 K as the monolayer is populated. Acetone molecules desorbing at 350 K constitute about 0.25 ML and exhibit H/D exchange with surface hydroxyl groups. On the other hand, coadsorbed water displaces about 0.75 ML of the acetone monolayer into physisorbed states, but does not influence the remaining 0.25 ML that constitutes the 350 K TPD peak. These strongly bound acetone molecules are not associated with oxygen vacancies. Virtually no photodecomposition is observed in the absence of gas phase O@sub 2@. Exposure to UV light in gas phase O@sub 2@ results in conversion of acetone to acetate via cleavage of a carbonyl-methyl bond. A similar reaction mechanism occurs in the dark during the coadsorption of acetone and molecular oxygen preadsorbed at oxygen vacancies, suggesting that acetone photodecomposition is facilitated through the excited electron channel (e.g., via reaction with an O@sub 2@@super -@ species) and not through oxidation by valence band holes. Photodesorption measurements reveal that the methyl group is ejected from the surface at 200 K but is retained on the surface at 100 K presumably by conversion into formate based on the absence of likely C@sub 1@ or C@sub 2@ species in TPD. The acetone photodecomposition cross section increases with increasing acetone coverage, but decreases with coadsorbed water. @FootnoteText@ This work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences.

3:40pm **SS1-WeA6 Water Adsorption on the Rutile TiO2(011)-(2x1) Surface*, A. Klust*,** *T.J. Beck, U. Diebold,* Tulane University*; C. DiValentin,* Universita' degli Studi di Milano-Bicocca, Italy*; A. Selloni,* Princeton University

Titanium oxide is a promising material for photocatalysis. Previous studies have shown that the photocatalytic activity of rutile TiO@sub 2@ depends dramatically on the surface orientation with the (011) surface being the most active.@footnote 1@ The TiO@sub 2@(011) surface forms a stable (2x1) reconstruction. Based on theoretical modelling and scanning tunneling microscopy (STM) studies, we propose a structural model for this surface. The surface is terminated by one-fold coordinated O atoms (titanyl groups), a feature that distinguishes it from all other known TiO@sub 2@ surfaces. We suggest that the titanyl groups are responsible for the high photocatalytic activity of the TiO@sub 2@(011) surface. Here, we present STM and ultraviolet photoemission (UPS) studies of water adsorption on the TiO@sub 2@(011) surface showing that water adsorb in both molecular and dissociative form at 110 K. First-principles calculations are in agreement with these results and provide detailed information on the structure of the adsorbed molecules. In contrast to the well - known (110) surface@footnote 2@, water dissociation is not mediated by surface defects demonstrating the high chemical activity of the TiO@sub 2@(011)-(2x1) surface. @FootnoteText@ @footnote 1@ G.S. Rohrer in: The Chemical Physics of Surfaces (2001), ed. D.P. Woodruff.@footnote 2@ I.M. Brookes et al. Phys. Rev. Lett. 87 (2001) 266103; R. Schaub et al. Phys. Rev. Lett. 87 (2001) 266104.

4:00pm **SS1-WeA7 Photoexcitation of TiO@sub 2@ and the Chemistry of Electrons and Holes***, **J.T. Yates, Jr.**,* University of Pittsburgh*; O. Diwald,* Technical University of Vienna, Austria*; D. Panayotov, T.L. Thompson,* University of Pittsburgh*; S.D. Walck,* PPG Industries*; T. Berger, E. Knözinger, M. Sterrer,* Technical University of Vienna, Austria **INVITED**

TiO@sub 2@ is a useful photocatalyst for the destruction of trace quantities of organic molecules in the environment. Photoexcitation of TiO@sub 2@ occurs as a result of electron-hole pair excitation by UV radiation with energy above the bandgap (3.0 eV). It has been found that N doping from NH@sub 3@ may be used to lower the photothreshold for TiO@sub 2@ by 0.6 eV, whereas N doping by ion implantation using N@sub 2@@super +@ leads to an increase in the photothreshold energy. Excited electrons in TiO@sub 2@ may be detected by EPR or IR spectroscopy, and hole formation in the valence band region may be detected by EPR as O@super -@ species. Excited electrons are observed to transfer to adsorbed O@sub 2@ to produce the O@sub 2@@super -@ species (superoxide). An adsorbed organic molecule, containing both S and Cl moieties has been shown to accept excited electrons when it is bonded to the surface by the Cl moiety, but not when bound by the S moiety, indicating that charge transfer occurs preferentially into the polyfunctional molecule by means of the more electronegative attachment group.

4:40pm **SS1-WeA9 +ACQ+AHs+Dye Sensitization of the TiO+AEA-Sub 2+AEA- polymorph Anatase (101) Single Crystal Surface by a Series of Dicarboxylated Thiacyanine Dyes+AHs+AH0-***, **N. Ruzycki**, S. Ushiroda, Y. Lu,* Colorado State University*; M.T. Spitler,* ChemMotif, Inc.*; B.A. Parkinson,* Colorado State University

+ACQ-Body +AHs-The dye sensitization of the TiO+AEA-Sub 2+AEA-polymorph anatase (101) is an important system of study because of its application to dye-sensitized solar cells such as the Gr+AEA-um A+AEA-tzel cell. The electrons per photon quantum yields for the dye sensitization of anatase are reported to be higher than those for the rutile polymorph of TiO+AEA-Sub 2+AEA-. The reason that anatase is a better substrate for photovoltaic purposes is yet unknown. The efficiency of solar cells is closely tied to the yield and rate of the electron transfer from the dye molecule to the surface, factors that will be influenced by the geometry of the dye binding and ordering at the surface. Studies that link UHV and electrochemical experiments are a first step towards understanding the mechanism of dye binding to the surface of this material. Dye sensitization of the single crystal anatase (101) surface was studied using a series of dicarboxylated thiacyanine dyes that bind to the surface through the carboxylate group. An ultraviolet (UV) light treatment of the anatase (101) surface, immediately prior to dye adsorption, improves both the reproducibility of dye coverage and the incident photon-to-current efficiencies (IPCE) for sensitization. The UV treatment does not pit or roughen the anatase surface and results in high IPCEs of up to 0.5 percent. The adsorption isotherms and adsorption and desorption kinetics of these dyes were studied. The photocurrent spectra showed features associated with surface-bound dye monomers, dimers and aggregates that could be followed as a function of the dye surface coverage. UHV studies on the single crystal anatase (101) surface were undertaken, including STM, for adsorption of a molecule (bis-isonicotinic acid) that had approximately the same backbone structure and carboxylate group as the dyes in order to elucidate structural models for the dye binding to the surface. +AEA.

5:00pm **SS1-WeA10 Enhanced Photocatalytic Activity in Fe@sub 2@O@sub 3@/Cr@sub 2@O@sub 3@ Epitaxial Heterojunctions***, **J.R. Williams**, S.A. Chambers, M.A. Henderson,* Pacific Northwest National Laboratory

The heterogeneous photocatalytic activity may be enhanced by the creation of an oxide-oxide heterojunction where the band alignment is such that photoexcited electron-hole pairs tend to separate at the interface, resulting in enhanced charge carrier lifetimes. Here we show that epitaxial heterojunctions of Fe@sub 2@O@sub 3@ and Cr@sub 2@O@sub 3@ do indeed exhibit enhanced photocatalytic activity relative to either pure material. The dependence of the enhancement on the heterojunction thickness will be discussed, as well as the wavelength dependence. The heterojunctions were grown on @alpha@-Al@sub 2@O@sub 3@ substrates by Oxygen Plasma Assisted Molecular Beam Epitaxy (OPA-MBE). Characterization by XPS and all photocatalysis experiments are performed in situ after growth with no air exposure at any time. Photocatalytic activity is measured by the extent of decomposition of trimethylacetic acid (TMA) adsorbed on the surface using a quadrupole mass spectrometer, XPS, and a Hg arc lamp with various filters as the excitation source. Specifically we have observed a factor of ~ 2-3 increase in photocatalytic activity for this type of heterojunction surface as compared to the same surface of either pure material.

Surface Science
Room 210C - Session SS2-WeA
Surface Collision Dynamics

Moderator: K.P. Giapis, California Institute of Technology

2:00pm **SS2-WeA1 Atomic-Scale Analysis of the SiH@sub 3@ Surface Reactivity During Plasma Deposition of Amorphous Silicon Thin Films***, **M.S. Valipa**, E.S. Aydil,* University of California, Santa Barbara*; D. Maroudas,* University of Massachusetts, Amherst

Hydrogenated amorphous silicon (a-Si:H) thin films grown by plasma-assisted deposition are used widely in the fabrication of solar cells and flat panel displays. The dominant precursor for deposition of device-quality a-Si:H films is the SiH@sub 3@ radical. Development of systematic strategies for depositing a-Si:H films with desirable properties requires a fundamental understanding of surface reactions of the SiH@sub 3@ radical leading to a-Si:H growth and H incorporation. This presentation focuses on detailed atomic-scale analysis of the surface reactions of SiH@sub 3@ using molecular-dynamics simulations of repeated impingement of SiH@sub 3@ radicals on growth surfaces of smooth a-Si:H films. The corresponding surface reaction probability, @beta@, is determined over the temperature (T) range 475-800 K. SiH@sub 3@ can either incorporate into the film by adsorbing onto a dangling bond or inserting into Si-Si bonds (sticking), or abstract surface H through Eley-Rideal (ER) or Langmuir-Hinshelwood (LH) pathways to produce SiH@sub 4@ gas, or react with another surface SiH@sub 3@ to desorb as Si@sub 2@H@sub 6@ (recombination), or leave the film by reflection or desorption. The overall @beta@ (sticking + recombination) is almost constant over the T range studied, as are the probabilities for sticking and recombination, s and @gamma@, respectively. Energetic analysis shows that SiH@sub 3@ adsorption and insertion and ER abstraction are barrierless processes, which explains the measured T independence of @beta@. LH abstraction is activated at high T, but competes with Si@sub 2@H@sub 6@ formation, yielding a T-independent @gamma@. Also, LH abstraction leads to H elimination from a-Si:H during growth and explains the T dependence of H content in the a-Si:H film.

2:20pm **SS2-WeA2 Adsorption Induced Phase Separation followed in Real Time by High-pressure Scanning Tunneling Microscopy***, **J. Knudsen**, R.T. Vang, E.K. Vestergaard, F. Besenbacher,* University of Aarhus, Denmark

The validity of surface science experiments as an efficient tool in catalysis research is often questioned due to the enormous difference in pressure conditions. For single metal systems the issue is most often concerned with the equivalence between adsorption phases obtained under low pressure and low temperature versus high pressure and high temperature phases. But for the case of more complex model systems such as bimetallic alloys the stability of the model catalyst becomes an additional important factor. We have developed a high-pressure fast-scanning STM which serves as an ideal tool for studies of high pressure induced morphological and structural changes in real time by the acquisition of STM movies. In this way we have been able to describe in great detail a CO induced phase separation of a Au/Ni(111) surface alloy. The STM movies reveal how a removal of nickel atoms from the topmost layer of the alloy surface is nucleated at the step edges of the surface. The gold atoms are left behind on the surface, and small gold clusters are formed in the wake of the moving step edge. Based on these experimental findings we propose a model, in which nickel atoms are removed by the formations of nickel carbonyls; a reaction that is well known from studies of clean nickel surfaces. Finally, we present recent studies of the stability of a Cu/Pt(111) surface alloy under high CO pressures. Exposure of the Cu/Pt(111) surface alloy to CO leads to the formation of clusters on the surface. The atomic details of this adsorbate-induced structural change of the Cu/Pt(111) alloy are currently being investigated.

2:40pm **SS2-WeA3 Quantum State Resolved Studies of Gas/Surface Reaction Dynamics***, **R.D. Beck**,* Ecole Polytechnique Federale de Lausanne (EPF), Switzerland **INVITED**

The dissociation of methane on a nickel catalyst is a key step in steam reforming of natural gas for hydrogen production. Despite substantial effort in both experiment and theory, there is still no atomic scale description of this important gas-surface reaction. To elucidate its dynamics, we have performed quantum state resolved studies of vibrationally excited methane reacting on the Ni(100) surface using pulsed laser and molecular beam techniques. We observed up to a factor of 5 greater reaction probability for methane-d2 with two quanta of excitation in one C-H bond versus a nearly isoenergetic state with one quanta in each of two C-H bonds. For CH4, stimulated Raman pumping is used to probe the reactivity of the totally symmetric C-H stretch vibration for comparison with reactivity of CH4 excited to the infrared active antisymmetric C-H stretch vibration. The observed reactivities point to a transition state structure which has one of the C-H bonds significantly elongated. Our results also clearly exclude the possibility of statistical models correctly describing the mechanism of this process and emphasize the importance of full-dimensional calculations of the reaction dynamics.

3:20pm **SS2-WeA5 Gas-Surface Reaction Dynamics at the Inorganic-Organic Interface***, **A. Dube**, P.F. Ma, A.S. Killampalli, M. Sharma, J.R. Engstrom,* Cornell University

Inorganic-organic interfaces play an important role in a number of technologies. Much of the work to date in the area of gas-surface reaction dynamics has involved study of the reaction of small organic molecules with transition metal surfaces. Here, we have chosen to examine the inverse problem: the reaction of coordination compounds of transition metals with model organic surfaces using supersonic molecular beam techniques. Such reactions are the first key step to barrier formation on organic surfaces, and they may result in a superior method for the formation of contacts to molecular electronics. In the work we report here we examine explicitly the reaction of Ti- and Ta- containing coordination compounds with a variety of self-assembled monolayers (SAMs) possessing different terminal endgroups (e.g.,-CH@sub 3@,-OH, -NH@sub 2@,-COOH), using both HX-R-SiCl@sub 3@/SiO@sub 2@ and HX-R-SH/Au based SAM chemistries. For example, for the reaction of Ti[N(CH@sub 3@)@sub 2@]@sub 4@ and for molecular kinetic energies E@sub i@ = 0.5-2.0 eV, we find that the reaction probability on -OH and -NH@sub 2@ terminated R-SiCl@sub 3@/SiO@sub 2@ type SAMs passes through a minimum, near E@sub i@ ~ 1 eV. Since we have shown in other work that penetration of the SAM by the coordination compound is possible, these results suggest that penetration is enhanced at sufficiently high E@sub i@. On the other hand, variation of both the substrate temperature and the angle of incidence indicates that reaction with these two terminal endgroups follows a trapping-mediated chemisorption channel. In selected cases we also make comparison to results from ab initio quantum chemistry calculations of the potential energy surface. For example, these calculations are consistent with a barrier near the vacuum level for the reaction on -OH terminated SAMs, which we observe experimentally, yet they suggest that reaction with an isolated -NH@sub2@ may be activated by as much as 15 kcal-mol@super -1@.

3:40pm **SS2-WeA6 Site-Selective Abstraction in the Reaction of 5- to 20-eV O@super +@ with a Self-Assembled Monolayer***, **X. Qin**, T.D. Tzvetkov, D.C. Jacobs,* University of Notre Dame*; D. Lee, L. Yu,* University of Chicago

The reaction of hyperthermal (5-20 eV) O@super +@ with alkanethiolate self-assembled monlayers (SAM) is studied under UHV conditions. To learn about the site-specificity to hydrogen abstraction in this system, we deposit SAM layers for which the hydrogen atoms located on the C-12, C-11, or C-10 positions of 1-dodcanethiol are substituted with deuterium atoms. By comparing the yields of OH to OD emerging from these three isotopomers, we find that hyperthermal O@super +@ initially abstracts only H(D)-atoms bound to the top two carbon atoms within the SAM layer. Continued bombardment with O@super +@ ions significantly disorders the structure of the SAM.

4:00pm **SS2-WeA7 Current Research and Development Topics on Gas Cluster Ion Beam Processes***, **I. Yamada**,* University of Hyogo, Japan**INVITED**

It has been 15 years now since the idea of the gas cluster ion beam (GCIB) process first came up, but the interest in GCIB process has increased only recently, driven by the nano-technology program, especially in Japan. This ion beam process uses a beam of ions consisting of clusters of a few hundreds to thousands of atoms generated from gaseous materials. The impact of these accelerated cluster ions with the surface produces a low energy bombardment at very high density. The cluster-surface collisions were found non-linear effects and to have unique characteristics which were found to be useful for applications in novel surface processing. These characteristics include surface effects such as shallow implantation, lateral sputtering, cleaning and smoothing, as well as low temperature thin film formation. This paper reviews the current fundamental research related to the GCIB-surface interactions as well as their applications in modern magnetic, optical and semiconductor device fabrications. These presently include: (i). IC Back End of the Line (BEOL) materials processing, (ii). surface smoothing of metals, dielectrics, superconductors, and diamond films for optical and magnetic devices, (iii). selective smoothing of SOI, SiC and compound semiconductor films and (iv). high quality thin multi-layer film deposition for reliable and durable optical filters.

Thin Films
Room 303C - Session TF-WeA

Transparent Conducting Oxides

Moderator: S. McEldowney, OCLI - JDS Uniphase

2:00pm **TF-WeA1 Structural, Electrical and Optical Properties of Transparent Conductive In@sub 2@O@sub 3@-SnO@sub 2@ Films***, **Y. Sato**, R. Tokumaru,* Aoyama Gakuin University, Japan*; K. Utsumi, H. Iigusa,* Tosoh Corporation, Japan*; P.K. Song, Y. Shigesato,* Aoyama Gakuin University, Japan

Transparent conductive In@sub 2@O@sub 3@-SnO@sub 2@ films were deposited by dc magnetron sputtering using high density ceramic targets which contained various SnO@sub 2@ contents (0-100 wt.%) on unheated glass substrates. These films were post-annealed under various atmospheres (Air, Ar or Ar+3%H@sub 2@) at 200 @super o@C for 1 hr. The structural, electrical and optical properties of these films were investigated. XRD profiles of all the as-deposited films exhibited amorphous structure. After post-annealing under various atmospheres, XRD profiles of the films deposited using targets of up to 20% SnO@sub 2@ contents showed bixbyte crystal structures of In@sub 2@O@sub 3@, whereas all the films deposited using the targets of SnO@sub 2@ contents higher than 20 wt.% showed amorphous structure. Resistivity of the films deposited using the targets of up to 20% SnO@sub 2@ contents was reduced from about 400 to 200 @micro@@ohm@cm by post-annealing under each condition, because carrier density increased with increasing the number of the substitutional Sn@super 4+@ at In@super 3+@ site as the result of the crystallization. All the post-annealed films possessed high transmittance of over 80 % in the region of visible light. In the region of over 1000 nm, the transmittance decreased with increasing Sn concentration, where reflectance increased. Work functions of the all films were analyzed by electron spectroscopy in air (ESA, AC-2). The work function of the films showed clear negative relationship to the carrier density. This could be explained in terms of the shift of the Fermi level to the higher energy in conduction band with the increasing carrier density.

2:20pm **TF-WeA2 Optimization of RF Magnetron Sputter Deposited Indium Tin Oxide (ITO) Transparent Conductors using a Taguchi Statistical Method***, **S.I. Jun**, P.D. Rack,* The University of Tennessee

In order to optimize the electrical and optical properties of ITO (indium tin oxide) thin films a statistical analysis called the Taguchi design was employed. The sputtering parameters that were considered included RF magnetron sputtering power, oxygen partial pressure, total sputtering pressure, and substrate temperatures. The responses that were considered included sheet resistance, transmission, deposition rate, and etch rate (in 22%HCl+6%CH3COOH+72%H2O). From this design of experiments it was determined that the sheet resistance and transmittance are inversely proportional to each other as a function of the process parameters. The preferred orientation of crystalline ITO film is distinguishably changed with an increase of sputtering temperature and oxygen fraction (O2/O2+Ar) in the sputtering ambient. The change in crystallinity results from the content of incorporated oxygen, which significantly affects the electrical and optical properties of ITO films and causes a rearrangement of atoms to form a preferred closed-packed plane orientation. Finally the microstructure of the ITO films becomes denser with increasing oxygen fraction. As a result of this work, we have successfully achieved low sheet resistance (7.0 ohm/sq.) and high transmittance (~90%) for our targeted 300nm thick films. In this presentation we will briefly review our design of experiments and illustrate our experimental procedure. Subsequently, we will discuss how each process parameter affects each measured response. Finally, will correlate the observed electrical and optical properties of the ITO films to the measured crystal structure and microstructure.

2:40pm **TF-WeA3 Optimization of Process Parameters to Achieve High Quality as-Deposited Indium-Tin Oxide Films for Display Applications***, **S. Gupta,*** The University of Alabama

High quality as-sputtered indium-tin oxide (ITO) films have been achieved by careful optimization of the process parameters@footnote 1@. Oxygen flow, deposition power, process pressure and deposition temperature were varied to achieve optimal resistivity and transmission characteristics of the ITO film. Resistivities below 300 µ@ohm@-cm and transmission of over 75% over most of the visible wavelength range of 400-800 nm, with a peak of 85% at about 550 nm, have been obtained for deposition temperatures below 180 @super o@C. For deposition temperatures of about 260 @super o@C, these numbers were improved to about 225 µ@ohm@-cm resistivity and over 90% transmission. The transmission numbers quoted are for the film plus the quartz substrate -- the film-only values exceed 95%. The thermal stability of the films was studied as a function of in-situ pre- and post-deposition annealing. It was seen that deposition of the ITO films at elevated temperatures improved thermal stability of the as-deposited films, and led to no further change in resistivity or transmission upon post-deposition annealing in atmosphere. ITO film properties vs. process parameters were also studied using two types of magnetron cathodes with maximum field strengths of a) 200 Oe, commonly used for non-magnetic materials, and b) 600 Oe, commonly used for magnetic materials. The purpose of changing cathode field strength was to determine whether lowering the plasma impedance by using a stronger field helped to lower the film resistivity, as reported by some researchers. We did not find any such correlation in our studies. @FootnoteText@ @footnote 1@ This study was performed at KDF, while the author was Director of Technology at KDF, 10 Volvo Drive, Rockleigh, NJ 07647.

3:00pm **TF-WeA4 Analysis on Thermal Properties of Tin-doped Indium Oxide Films by Picosecond Thermoreflectance Measurement***, **T. Yagi,** K. Tamano, Y. Sato,* Aoyama Gakuin University, Japan*; N. Taketoshi, T. Baba,* National Metrology Institute of Japan*; Y. Shigesato,* Aoyama Gakuin University, Japan

First time attempt of observation of thermal diffusion across tin doped indium oxide (ITO) thin films perpendicular to the film plane has been carried out using a picosecond thermoreflectance measurement@footnote 1@. ITO films sandwiched by molybdenum (Mo) films were prepared on fused silica substrate by rf magnetron sputtering using ITO and Mo multi-targets. Such Mo/ITO/Mo layered structure was fabricated without exposure to the atmosphere between each deposition. The Mo films with thickness of 70 nm are necessary because the wavelength of pulse laser used in this study is 780 nm at which wavelength ITO is transparent. The ITO films with different thickness of 30, 50 and 70 nm were prepared as the intermediate layer in order to estimate thermal resistance at the interface between Mo/ITO. The resistivity, carrier density and Hall mobility of the ITO film was 4.2e-4 ohm cm, 3.5e20 cm@super -3@ and 35 cm@super 2@/Vsec, respectively. The interface between the Mo films and the fused silica substrate was irradiated by picosecond laser pulse (2 ps). Heat generated by the pump laser pulse diffuses toward the top Mo surface across the three-layered films. Then the temperature changes at the Mo film surface, which was probed by reflectivity of another picosecond laser pulse. The thermal diffusion time increased with the increase in the thickness of the ITO layers. The thermal diffusion coefficient of the ITO films and thermal resistance at ITO/Mo were found to be 3e-6 m@super 2@/s and 1e-8 mK/W, respectively. This research was supported in part by the New Energy and Industrial Technology Development Organization (NEDO) in Japan. @FootnoteText@ 1: N. Taketoshi, T. Baba, E. Schaub, A. Ono: Rev. Sci. Instrum., 74, (2003), pp. 5226-5230.

3:20pm **TF-WeA5 Direct Observation of Hydrogen Generated Free Carriers in ZnO Thin Films***, C.A. Wolden,* Colorado School of Mines*; J.B. Baxter,* University of California Santa Barbara*; T.M. Barnes,* Colorado School of Mines*; E.S. Aydil,* University of California Santa Barbara

Zinc oxide is a versatile wide band-gap semiconductor that has generated tremendous interest due to its unique combination of optical, electronic and mechanical properties. Hydrogen is common to many ZnO processing environments, and recent first principle calculations have suggested that it behaves exclusively as an electron donor in ZnO. Although hydrogen in ZnO has been observed in bulk single crystals, its behavior has not been examined in commonly used polycrystalline thin films. We report on the use of in situ attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy to probe the changes in free carrier absorption when thin ZnO films are exposed to H or O atoms generated by H@sub 2@ and O@sub 2@ plasmas, respectively. Polycrystalline ZnO films were deposited on ATR crystals using metalorganic chemical vapor deposition or a plasma-assisted CVD technique. For both types of films, room temperature exposure to hydrogen plasma resulted in a sharp increase in free carrier infrared absorption and free carrier density. Carrier concentrations and mobilities were extracted from the infrared spectra using a model for the complex dielectric function. Hydrogen uptake was rapid and the carrier concentration reached its saturation level (~10@super 18@ /cm@super 3@) in less than a minute of H@sub 2@ plasma exposure. Room temperature oxygen plasma exposure of the hydrogenated films decreased free carrier absorption, but this decrease was only a fraction of the free carrier density increase after H exposure. Extended exposure to oxygen plasma at elevated temperatures (~200°C) was required to return the carrier concentration to levels that are comparable to those in the as-deposited films. The results are contrasted with observations from single crystal experiments, and the ramifications for device processing are discussed.

4:20pm **TF-WeA8 A Note on the Measurement of Carrier Density by Hall Effect in p- Type Transparent Conducting Oxide (TCO) Thin Films***, **A. Subrahmanyam,*** Indian Institute of Technology Madras, India

P- type transparent conducting oxide (TCO) thin films are the emerging new materials with a vast potential in transparent electronics. Many research groups are working on the preparation and characterization of these films but with a limited success. The Silver Indium oxide (AIO) and Copper Aluminum oxide (CAIO) belonging to the Delafossite crystal structure have shown p- type conductivity, however, the preparation conditions have a very narrow window for the growth parameters to realize p- type conduction. These materials being metal oxides, any small oxygen deficiency leads to metal rich films with sufficient free electrons. Thus, there exists a bipolar conduction in these p-type TCO films. The conventional Hall effect measurement with bipolar conduction (with comparable free carrier concentrations) and the electrons and holes having different mobilities leads to an incorrect sign of the Hall coefficient and erroneous estimation of the majority carrier concentration. In the present paper, Hall effect data from several groups (including the author's group) on several thin films (prepared with different growth conditions) of silver indium oxide (AIO) and copper aluminum oxide (CAIO) have been analyzed. The analyses clearly reveal that a lot of caution is to be exercised while measuring and interpreting the Hall effect data. The concept of Quantitative Mobility Spectrum Analysis (QMSA) for evaluating the mobility and carrier concentration in bipolar semiconductors is discussed in light of the TCO thin film samples. The contact potential difference (CPD) measurements by Kelvin probe technique to estimate the work function (and thus the Fermi level) in these p- type TCO thin films seems to be one of the potential techniques to estimate the p- type nature of conduction.

4:40pm **TF-WeA9 Electrical and Optical Properties of Reactive DC Magnetron Sputtered Silver Doped Indium Oxide Thin Films***, **S. Srinivasan,** A. Subrahmanyam, B. Ullash Kumar,* Indian Institute of Technology, India*; C.L. Nagendra,* Indian Space Research Organization (ISRO), India

In the present study, the role of oxygen in the formation of semiconducting Silver doped Indium oxide thin films is reported. This material has potential application in opto-electronic devices. The Silver doped Indium oxide thin films have been prepared on quartz and soda lime glass substrates at room temperature (300 K) by reactive DC Magnetron sputtering technique. The target is a pure Silver: Indium metal of composition 5: 95 At %. The oxygen flow rates in the growth chambers have been varied in the range of 12.5-14.0 sccm. The sputtering power is kept constant at 50 watts. The X-ray diffraction pattern shows the amorphous nature of these thin films. The electrical resistivity measured at room temperature increases (2.158Ã-10-2 â?"1.545Ã-10-1 â"¦-cm) with increasing oxygen flow rates. The films show an n-type behavior as shown by the Hall effect measurements. The Hall mobility is observed to be decreasing (12.071- 1.984 cm2v-1s-1) with increasing the oxygen flow rates. The thickness and refractive index of these films have been measured by using a spectro-photometric technique and the associated computation algorithm. The thickness of the film as determined by the technique is in the range 165-220 nm. The refractive index and absorption index of these films varies in the range 1.9- 2.1 and 0.01-0.02 over the spectral range from 2500-400nm. The work function has been measured on these films by contact potential method using Kelvin Probe. These data are being analyzed for an understanding of transport mechanism of these films.

Vacuum Technology
Room 303D - Session VT-WeA

Vacuum Measurement, Sensors and Control

Moderator: T. Gessert, National Renewable Energy Laboratory

2:00pm **VT-WeA1 An Overview of Particle and Field Instruments to Measure Solar System Plasma*, M. Wüest,*** Astroglobo, Switzerland

For almost 50 years solar system plasma has been studied by in-situ as well as remote sensing instruments. These instruments include particle instruments such as different kinds of mass spectrometers, solid state detectors or neutral atom imagers as well as electromagnetic field measuring instruments such as magnetometers and electric field instruments. In this presentation I will give an overview of the different types of instruments used in space research to better understand the plasma environment of the solar wind and the planetary magnetospheres.

2:20pm **VT-WeA2 An Overview of the Spallation Neutron Source Vacuum Systems*, P. Ladd,*** Oak Ridge National Laboratory **INVITED**

The Spallation Neutron Source (SNS) is an accelerator-based neutron source being built in Oak Ridge, Tennessee funded by the U.S. Department of Energy (DOE) Office of Science. The SNS will provide the most intense pulsed neutron beams in the world for scientific research and industrial development. At a total cost of $1.4 billion, construction which began in 1999 and will be completed in 2006 the culmination of the collaborative efforts of six National Laboratories (Argonne, Brookhaven, Jefferson, Lawrence Berkeley, Los Alamos, and Oak Ridge). Powerful neutron beams will be produced in the SNS facility by bombarding a mercury target with energetic protons from a large accelerator complex. A UHV environment is needed in the accelerator to minimize beam losses as the beam is accelerated from the ion source, where low energy particles are produced, through a series of accelerating cavities eventually accelerating the beam to 88% the speed of light with a capable of depositing 1.4 MW on the target at a beam energy of 1 GeV. The component parts of the accelerator will be briefly described specifically addressing the design and construction of the numerous vacuum systems that support accelerator operations. In conclusion the current status of the installation and commissioning of the various vacuum systems will be presented.

3:00pm **VT-WeA4 Interactions of Various Vacuum Gauge Sensor Technologies with their Measurement Environment*, P.M. Rutt,*** Helix Technology Corporation

The effects of industrial processing atmospheres on the operating components of a number of vacuum gauge sensor technologies are presented. Each common type of vacuum gauge sensor is evaluated with respect to its functional components. The gauges considered are hot cathode ionization gauges, cold cathode ionization gauges, various material diaphragm gauges, and thermal conductivity gauges. The mechanisms evaluated with respect to the gauge internal electrodes/sensors are erosion, chemical interaction, metallurgical interactions, and deposits. Some of these component problems will be addressed with possible solutions.

3:20pm **VT-WeA5 Modulated Bayard-Alpert Gauges in a Calibration Laboratory*, B.R.F. Kendall,*** Elvac Laboratories*; E. Drubetsky,* The Fredericks Company

Bayard-Alpert (BA) gauges may have large errors at pressures below about 10@super -9@ Torr because of x-ray and other unwanted effects. One of the simplest ways to overcome these problems is to add a modulator electrode, as described by P.A. Redhead in 1960. At least a factor of ten improvement in minimum detectable pressure is possible. We describe operational experience with both nude and metal-envelope modulated BA gauges on two UHV systems operating in the 10@super -11@ Torr range. In addition to eliminating x-ray errors, these gauges proved to have numerous other advantages which have not been generally recognized. They are unaffected by electrometer zero drift and are capable of discriminating against spurious currents caused by electron-stimulated ion desorption. Standard commercial ion gauge controllers can be used, with the addition of simple external adapters. These can range from elementary manually-operated switches giving single readings of true pressure, up to programmable devices capable of giving continuous readouts of true pressure and the magnitudes of the various error signals. A gauge tube with a modulator electrode can also be used, if necessary, as a conventional BA gauge with a standard controller simply by connecting the modulator to the electron collector (i.e. to the grid). We are replacing most of the conventional BA gauges on our UHV systems with modulated gauges. This has eliminated over-readings which sometimes approached 300 percent of true pressures in the mid 10@super -11@ Torr range.

3:40pm **VT-WeA6 Considerations for Selection of Ion Collector Diameter in Hot Cathode Ionization Gauges*, P. Arnold,*** Helix Technology Corporation

Characteristics of large diameter vs small diameter ion collectors in Bayard-Alpert type hot cathode ionization gauges are evaluated. Experimental data are shown for high pressure linearity, high pressure stability, and multi-second pumpdowns from the millitorr range to the high vacuum range. These pumpdowns were conducted with both argon and nitrogen as functions of time, pressure, and electron emission current in the millitorr range. Computer simulations and mathematical calculations are related to the test data to arrive at an explanation of the observed results. This evaluation is extended to miniature hot cathode gauges.

4:00pm **VT-WeA7 A Study of the Variation of Sensitivity of Hot Cathode Ionization Gauges as a Function of Gas Adsorption*, P.J. Abbott,*** National Institute of Standards and Technology*; P. Mohan,* National Physical Laboratory, India

Hot cathode ionization gauges of the Bayard - Alpert design are the most widely used gauges for pressure measurement in the high and ultra high vacuum range. The National Institute of Standards and Technology (NIST), has considerable experience in calibrating hot cathode ionization gauges of this type for customers and for its own use. Several different envelope geometries have been encountered for example, nude gauges, gauges with glass envelopes, and the more recent gauges having metal envelopes. The sensitivity of this particular type of metal envelope ion gauge is claimed to be highly repeatable, typically within a few percent over the period of one year. However, we have noticed much larger sensitivity shifts in these gauges during routine operation. We report the results of a systematic study of the change in sensitivity for two glass envelope ionization gauges, six metal envelope ionization gauges, and one extractor gauge over the pressure range 2x10@super -@@super6@ Pa to 7x10@super-@@super3@ Pa. An orifice flow (dynamic expansion) system generated the nitrogen and argon calibration pressures, and a spinning rotor gauge was used as a check standard for pressures above 10@super-@@super3@ Pa. For both argon and nitrogen, we found each gauge's sensitivity to be dependent on the quantity of gas the operating gauge was exposed to prior to calibration, i.e., the product of pressure and time. For argon gas, sensitivity shifts of up to 8 % were observed between an initial calibration and one performed after exposing the gauges to 0.028 Pa of argon for about five hours. For nitrogen, the shifts were as large as 14 %. Interestingly, for argon the sensitivity shifts occur towards the high-pressure end of the calibration range, while for nitrogen the shifts occur at the low pressure range. We believe that ionic pumping of gas and its subsequent release by the walls of the metal envelope is responsible for the observed sensitivity shifts.

4:20pm **VT-WeA8 A Study of Some Metrological Characteristics of Capacitance Diaphragm Gauges*, P. Mohan,*** National Physical Laboratory, India

The capacitance diaphragm gauges (CDGs) have been in use for a few decades and have been employed as transfer standards and reference standards. Despite their drawbacks, they continue to be used due to their ruggedness and UHV compatibility. A CDG consists of a sensor and an electronics control unit to display the pressure. To overcome the problem of ambient temperature variations, a heater is provided in the sensor to maintain it at nominally 45 °C. In a differential CDG, zeroing is done with both sides kept under vacuum. Afterwards, the system check (SC) is performed. This parameter is compared with the value given in the calibration sheet. A deviation between the two values is an indicator of the gauge needing re-calibration. A study has been performed to establish the link between the calibration factor (CF) and the SC, between the SC and the temperature of the CDG sensor and between the temperature and the shift in the sensor zero. A Resonant Silicone Gauge of 130 kPa f.s. range was used as a secondary standard for the calibration of the CDGs. The plots of CF against the pressure at different temperatures show that over a range of pressures, typically 100-1000 torr, the CF varies linearly with pressure and both the slope and the intercept values of this linear fit go on increasing as the temperature increases from about 290 - 318 K. Each temperature value corresponds to a different value of the SC. At 318 K, the CF tends to become a constant over the pressure range 100-1000 torr, meaning thereby that the slope becomes zero. Hence it can be said that the slope and intercept of the CF vs. pressure curve are a function the SC. Plots of the different values of the slope and the intercepts against the SC values give linear fits from which we can calculate the slope and the intercept values for any particular SC value. Hence we can calculate the CF at any pressure in the range 100-1000 torr, for any temperature between 290-318 K.

4:40pm **VT-WeA9 Ultra-sensitive Leak Detection during UHV Evacuation by QMS under Accumulate Mode***, X. Chen, L. Wang,* ***T. Huang****, Q. Jin,* Tsinghua University, China*; L. Cha,* Tsinghua University, China, P. R. China

Tightness is extremely important to guarantee the longevity of the sealed vacuum devices with smaller volume, especially if it has to maintain high vacuum or even ultra high vacuum (UHV). As the structure of such minimized UHV devices is developed to be more complicated, it becomes a serious challenge to the leak detection technology. According to the basic concepts of the modern leak detection engineering, each part of the device and their whole assembly should be passed leak detection strictly before UHV evacuation. However, the long term baking during the UHV evacuation may cause formerly plugged mini leakage reopen or produce some new mini leakages. In order to improve the tightness reliability of such devices, it is necessary to carry out ultra-sensitive leak detection during the UHV evacuation, especially just before the device be sealed off from the vacuum system. The quadrupole mass spectrometer (QMS) in the UHV evacuation system can be used under accumulate mode to solve this problem. After the long term baking, the UHV will be achieved and the background will be very low if there are no large leaks. Under such condition, the leak detection sensitivity of QMS is high enough to detect small leaks. By closing the all-metal valve in front of the tested device to accumulate helium for a period, a peak can be observed by QMS when the valve reopen if there are mini leakages. The ultra-sensitive leak detection can be achieved by this way. It is found that the open action of the metal valve always severely affects the height of the peak indicated by QMS to bring considerable errors. If denote the mini leakage by the peak area instead of the peak height, the situation will be much improved. It has been proven that this method is quite useful to ensure the tightness quality for the complex sealed UHV devices with small and mini volume.

5:00pm **VT-WeA10 The Spinning Rotor Gauge: From Laboratory Curiosity to Practical Tool***,*

First laboratory investigations on using magnetically suspended rotors for vacuum pressure determination were carried out by Jesse W. Beams and co-workers in the 1940s at the University of Virginia, Charlottesville.@footnote 1@ The suspension system was recognized as useful also for the investigation of a special drag effect on high-speed rotors due to retarded gravitational force interaction as proposed by James C. Keith in 1963.@footnote 2@ For experimental verification of the Keith effect,@footnote 3@ a permanent-magnet suspension was developed in the late 1960s at the University of Bonn that later on provided the technological basis for a first practical SRG. The SRG development was initiated and supported among other magnetic suspension applications, such as turbomolecular pumps, neutron and molecular beam choppers, by George Comsa at KFA Juelich since 1974. Extensive studies by G. Messer at PTB-Berlin and other leading national standard laboratories, in particular the American National Bureau of Standards, in the late 1970s have prepared the way for commercialization of the SRG. A theory on the influence of the rotor surface roughness on the SRG calibration was proposed in 1980.@footnote 4@ Significant technical improvements have been contributed by Bernd Lindenau, KFA-Juelich, and Klaus Witthauer, RWD-Aachen. On occasion of the IVC-8 exhibition in Cannes (1980), MKS Instruments was the first company to apply for licence from KFA-Juelich, followed by Leybold AG in 1981. The commercial units were manufactured on order of the licensing companies by RWD-Aachen. Extension of the SRG operating range beyond the molecular drag regime up to atmospheric pressure was introduced in the mid 1980s and first commercialized by SAES Getters in 1996. @FootnoteText@ @footnote 1@J. W. Beams, J. L. Young, J. W. Moore, J. Appl. Phys. 17, 887 (1946) @footnote 2@ J. C. Keith, Rev. Mex. Fis. 12, 1 (1963) @footnote 3@ J. K. Fremerey, Phys. Rev. Lett. 30, 753 (1973) @footnote 4@J. K. Fremerey, Proc. 4th ICSS and 3rd ECOSS, vol. II, p.869, Cannes (1980)

Science of Semiconductor White Light Topical Conference Room 304B - Session WL+MS-WeA

Science of Semiconductor White Light II

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

2:00pm **WL+MS-WeA1 Material and Device Challenges of Deep UV Emitters***,* ***M.H. Crawford****, A.A. Allerman, A.J. Fischer, K.H.A. Bogart, S.R. Lee, W.W. Chow,* Sandia National Laboratories **INVITED**

One of the new frontiers of light emitting diode research is the application of wide bandgap AlGaN alloys to achieve electroluminescence at 300 nm and shorter wavelengths. While most near-UV (380-400 nm) LEDs employ InGaN quantum well structures with GaN barriers, reaching deep UV wavelengths requires the growth of AlGaN alloys with aluminum concentrations of 50% and higher. In this presentation, we will review the present status of LED technology in the deep UV range and will discuss in detail the material and device challenges for achieving high performance devices. We will present data on LEDs that are grown by metal-organic vapor-phase epitaxy and employ flip-chip device geometries. These devices have yielded > 1 mW output powers in the 275-290 nm range under DC current operation. Critical device issues that will be discussed include performance under pulsed current injection, device lifetimes and an evaluation of the origins of deep level emission in the electroluminescence spectra. Electroluminescence at wavelengths shorter than 250 nm will be presented, and limitations of short wavelength performance will be discussed. Sandia is a multiprogram laboratory operated by Sandia Corporation for the United States Department of Energy's National Nuclear Security Administration under Contract DE-AC04-94AL85000. This work is supported by DARPA under the SUVOS program.

2:40pm **WL+MS-WeA3 Interfaces in White Light-Emitting Structures***,* ***P.H. Holloway,*** University of Florida **INVITED**

Solid state devices have the promise to revolutionize the generation of white light. Solid state lighting has the potential to increase the efficiency of converting electricity to light by factors of two or more. The solid state structures are robust and hint at lifetimes of thousands of hours. Interfaces in these devices will play an important role in the fulfillment or collapse of this promise. The best performance to date has been achieved with light emitted from GaN-based LEDs which contribute a blue component to the emitted light, while simultaneously photo-pumping one or more phosphors which luminescence to provide a color spectrum with a good color rendering index. Critical interfaces in these structures range from the interfaces between the epitaxial layers, to the metal-semiconductor interfaces for ohmic contacts, to the matix-phosphor interface for light scattering and quenching luminescence. Our knowledge about these types of interfaces will be illustrated using examples of interfacial characterization and reactions, and the need for new understanding will be illustrated.

3:20pm **WL+MS-WeA5 Ohmic Contacts to (Al)GaN Semiconductors for Light Emitters***,* ***I. Adesida,*** University of Illinois at Urbana-Champaign **INVITED**

The direct bandgap of GaN-based semiconductors have made them attractive materials for the realization of a wide range of optoelectronic devices. Examples of devices that are either commercially available or have been demonstrated include short wavelength light emitting diodes (LEDs), solar blind detectors, and laser diodes which have applications in white light illumination, bio-chemical agent sensing, solar UV detection, missile detection, flame and heat sensing, ozone monitoring, and remote sensing. Materials growth and device processing are still critical issues in terms of obtaining highly efficient GaN-based optoelectronic devices. The realization of highly reliable, thermally stable, low resistance ohmic contacts to both n-type and p-type GaN-based semiconductors is essential. To date, the formation of contacts to AlGaN with high Al concentration remain a challenge for various reasons. In this paper, we will describe our work on ohmic contact formation on both n- type and p-type AlGaN of various Al concentrations. Results on n-type contact formation using various metallization schemes will be presented. Contact formation to p-type AlGaN using Pd-based metallization schemes will be presented. Issues of thermal stability of these contacts will be discussed. The efficacy of various surface treatment schemes for GaN and AlGaN to improve the ohmic performance of the contacts will be discussed. Comprehensive studies are being performed to compare the effects of various surface treatment schemes which include both plasma and wet processes on the electrical and material characteristics of GaN and AlGaN semiconductors. Further, the mechanism of formation of ohmic contacts in these semiconductors will be discussed.

4:00pm **WL+MS-WeA7 Passivation and Processing-Induced Changes in GaN/Insulator Interfaces***, **R.J. Nemanich**, T.E. Cook, Jr., C.C. Fulton, W.J. Mecouch, R.F. Davis, G. Lucovsky,* NC State University **INVITED**

Passivation of GaN and AlGaN surfaces is now a critical limitation in electronic device fabrication. The band relations of various dielectrics on III-nitrides are just being established, and some interfaces show significant process induced variations. The characteristics of clean n- and p-type GaN (0001) surfaces and the interface between this surface and SiO2, Si3N4, and HfO2 have been investigated. Layers of SiO2, Si3N4, or HfO2 were carefully deposited to limit the reaction between the dielectric and the clean GaN surfaces. After stepwise deposition, the electronic states were measured with x-ray photoelectron spectroscopy (XPS) and ultraviolet photoemission spectroscopy (UPS). A valence band offset (VBO) of 2.0 eV with a conduction band offset (CBO) of 3.6 eV was determined for the GaN/SiO2 interface. For the GaN/Si3N4 interface, type II band alignment was observed with a VBO of 0.5 eV with a CBO of 2.4 eV, which differs substantially from prior reports. We suggest that the differences are related to the level of oxygen incorporated at the interface. A VBO of 0.4 eV with a CBO of 2.0 eV was determined for the GaN/HfO2 interface. An instability was observed in the HfO2 film, with energy bands shifting ~0.5 eV during a 650Â°C densification anneal. The deduced band alignments were compared to the predictions of the electron affinity model and deviations were attributed to a change of the interface dipole. The largest deviation was observed for the oxide layers. It was noted that the existence of Ga-O bonding at the heterojunction can significantly affect the interface dipole, and consequently the band alignment in relation to the GaN.

4:40pm **WL+MS-WeA9 Emissivity-Correcting Pyrometry for Group-III Nitride MOCVD***, **J.R. Creighton**, C.C. Mitchell,* Sandia National Laboratories **INVITED**

Accurate temperature measurement during group-III nitride MOCVD is very 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. We have developed a pyrometer that operates near the high-temperature bandgap of GaN, thus solving the transparency problem once a ~1 micron thick GaN epilayer has been established. At typical GaN MOCVD conditions the RMS temperature noise of the system is <0.1°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. Using this method we have measured the high temperature optical constants of GaN at the effective pyrometer wavelength (405 nm). Near 1000°C, the imaginary part (k) of the GaN refractive index is ~0.2, thus demonstrating that the epilayer is opaque. Small artifacts (due to stray light) in the emissivity-correction method are often observed, leading to residual oscillations in the corrected temperature. For our new nitride pyrometer the residual temperature oscillations are typically <3°C in amplitude when growing AlN/GaN heterostructures. Through proper calibration experiments, the nature of the error can be understood and quantitatively eliminated. We will also report on our recent efforts to extend this nitride pyrometer technology to multiwafer MOCVD reactors. (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.).

Thursday Morning, November 18, 2004

Applied Surface Science
Room 210A - Session AS-ThM

High-k Dielectrics

Moderator: D.R. Baer, Pacific Northwest National Laboratory

8:20am **AS-ThM1 Physical and Chemical Characterization of MOCVD Zirconia Films Deposited on Hydrogen-Terminated and Native Oxide Si Surfaces*, B.R. Rogers,*** Vanderbilt Universirty*; Z. Song, R.D. Geil, R.A. Weller,* Vanderbilt University*; M.O. Bloomfield, T.S. Cale,* Rensselaer Polytechnic Institute

Successful replacement of silicon dioxide-based MOSFET gate dielectrics by a high-permittivity (high-k) dielectric is a critical step in the continued drive to build the smaller, faster, lower-power, more-integrated circuits that society is demanding. Our group has been studying zirconia films deposited via MOCVD on hydrogen terminated silicon and silicon native oxide surfaces. Process pressures on the order of 10@super -5@ torr were used along with substrate temperatures between 300 and 450 @degree@C. Films were characterized using AFM, TEM, AES, spectroscopic ellipsometry, time-of -flight medium energy backscattering, and XRD. Results show that films deposited on hydrogen-terminated silicon are rougher, and have a mainly tetragonal microstructure. In contrast, films deposited onto silicon native oxide are much smoother and have a mixture of tetragonal and monoclinic microstructure, the ratio of the two microstructures depended on the deposition temperature. In addition, grain sizes in films of similar thickness also depended on the surface on which the films were deposited. In situ spectroscopic ellipsometry analyses show that depositions on hydrogen-terminated silicon begin with and induction period (where no deposition occurs) followed by a linear growth. Depositions on silicon native oxide have no induction period, initiating immediately into linear growth. Results from additional analysis techniques, along with simulation of the nucleation/growth process provide insight into the reason why films of different properties are deposited onto the two surfaces. This work is supported by the National Science Foundation grant # CTS-0092792.

8:40am **AS-ThM2 Challenges for the Characterization and Integration of High-k Dielectrics*, R.M. Wallace,*** University of Texas at Dallas **INVITED**

The integration of advanced gate dielectric materials into CMOS technology presents several significant challenges.@footnote 1,2@ Moreover, the introduction of these materials is expected to occur at an unprecedented pace to meet industry technology forecasts. Although recent research has focused on the search for a material that yields a suitable (higher) dielectric constant than the industry benchmark SiO@sub 2@, a more important problem is the actual integration of any new dielectric material in existing CMOS flows in a cost-effective manner. These integration issues include etching, constituent stability, control of phase segregation and crystallization, dopant penetration, as well as gate electrode compatibility, which influence the resultant electrical properties. The study of these issues require substantial efforts in physical and electrical characterization. This talk will examine several of these integration issues in view of recent characterization studies and the associated challenges that must be addressed for successful high-k gate dielectric integration. This work is supported by the Texas Advanced Technology Program. @FootnoteText@@footnote 1@G.D.Wilk, R.M.Wallace and J.M.Anthony, J. Appl. Phys., 89, 5243 (2001). @footnote 2@R.M.Wallace and G.D.Wilk, Crit. Rev. in Sol. State Mat. Sci, 28, 231 (2003).

9:20am **AS-ThM4 Engineering the Properties of Hf-based Gate Dielectrics: Role of Initial Surface Preparation and Post Deposition Annealing***, R. Puthenkovilakam,* ***Y.-S. Lin,*** *J.P. Chang,* University of California, Los Angeles

Alternative gate dielectrics such as HfO@sub 2@ or HfO@sub x@N@sub y@ are required in the future generations of MOSFET devices to enable their rapid down-scaling. However, the material and electrical properties of these materials are not fully understood or optimized. In this work, we investigate the material and electrical properties of ultra thin HfO@sub 2@ and HfO@sub x@N@sub y@ films on Si, deposited by an atomic layer controlled deposition process involving alternate pulses of Hf-t-butoxide precursor and oxygen (or NH@sub 3@). Post deposition annealing was performed in-situ in O@sub 2@, N@sub 2@, N@sub 2@O, NH@sub 3@ and ex-situ in H@sub 2@/D@sub 2@. X-ray photoelectron spectroscopy (XPS) measurements indicated the formation of interfacial layer and its structural changes upon post-deposition will be addressed. Extended x-ray absorption fine structure (EXAFS) measurements indicated that the short-range order in the as-deposited HfO@sub 2@ films resembled to that of the monoclinic phase HfO@sub 2@ and showed signs of crystallization upon annealing, while N incorporation seems to change the short-range order in the films and increase the crystallization temperature. Capacitance-voltage (C-V) measurements were performed on MOS devices to extract the dielectric constants (k), flat band voltage shifts, and interface state density. The as-deposited samples yielded k-values from 15-23 and their leakage currents were significantly less than that of SiO@sub 2@ films at the same equivalent oxide thickness (EOT). Temperature dependent current-voltage (I-V) measurements were performed to elucidate the conduction mechanisms in these ultra thin films. Substrate injection resulted in Schottky-like current transport while the gate injection showed a tunneling mechanism. The effect post-deposition annealing on the electrical performance will also be addressed in this talk in detail.

9:40am **AS-ThM5 Applications of ARXPS to Semiconductor Fabrication and Characterization*, P. Mack*,** *M. Shakespeare, A. Wright, R.G. White,* Thermo Electron Corporation, UK

In modern semiconductor fabrication, two trends are clear. Layers are becoming thinner and the materials are becoming chemically more complex. For these reasons, XPS is becoming increasingly important as a characterisation tool. It is well known that XPS provides chemical state information from the near surface region and commercial tools exist to handle wafers of up to 300 mm. Now that the thickness many of the layers used in semiconductor technology are less than the escape depth of the photoelectrons, the technique can be used to characterise the layers and their interface with the substrate. If angular resolution is combined with the XPS technique (angle resolved XPS or ARXPS) it becomes possible to measure the thickness of layers, and the distribution of the materials and chemical states within the layer non-destructively. For example, not only can ARXPS measure the thickness of an oxynitride layer but it can also determine the way in which nitrogen is distributed through the layer. The nitrogen distribution affects both the electrical properties and the accuracy of dose measurements. In the case of high-k dielectrics, the nature and thickness of both the high-k layer and any intermediate silicon dioxide or silicate layer can be determined. The combined electrical properties of these layers determine the integrity of the dielectric stack. By using the technique of parallel ARXPS it becomes possible to make all of these measurements from intact 300 mm wafers. ARXPS can produce depth profiles without the need for sputtering. This means that ARXPS has the potential to be applied to shallow implants, such as arsenic in silicon. This has the advantage over SIMS profiles that it does not suffer from near-surface sensitivity artefacts. Examples of materials characterisation from a range of semiconductor thin films will be shown.

10:00am **AS-ThM6 ALD and MOCVD Growth of High K Dielectric Al and Hf Films Studied by Parallel Angle Resolved XPS (PARXPS)*, R.K. Champaneria,*** Thermo Electron Corporation, UK, England*; P. Mack, J. Wolstenholme, R.G. White,* Thermo Electron Corporation, UK

XPS has been identified as being a suitable technique for the characterisation of surfaces and ultra thin layers encountered in semiconductor device fabrication. The extension of this technique to angle resolved XPS, ARXPS allows quantification of elemental and chemical state concentrations in the region of 5 to 10nm, a thickness that is well matched with the gate dielectric thickness currently used. By using maximum entropy calculations it is possible to generate non-destructive atomic concentration depth distribution plots from ARXPS data. These plots show the integrity of a film as well as the behaviour of interfacial layers. This paper looks at Al and Hf films grown by ALD and MOCVD processes. It shows differences in the state of the grown or deposited film as well as changes to the interfacial layer depending on how the film is grown and the thickness of the film. In addition, surface pre-treatment is also found to have a dramatic affect on the nature and role of the interfacial layer For Al and Hf multilayer films the integrity, thickness, preferential growth and the role of the interfacial layer are also investigated.

10:20am **AS-ThM7 Comparative Study of Metal Oxy-Nitride Films by Electron Spectroscopy***, P.M. Mrozek,* ***D.F.A. Allgeyer,*** *B.C. Carlson, K.B. Beaman, H.K. Krasinski,* Micron Technology, Inc.

X-ray photoelectron spectroscopy (XPS) was used extensively to provide information regarding the chemical composition and chemical states of the nitrogen in silicon, hafnium, and other oxy-nitride films grown on silicon or tungsten substrates. Different substrates were investigated in order to minimize differential charging effects. Nitride and ON-like states were identified in different films, and their depth distributions were found to vary from film to film. Nondestructive angle-resolved XPS analysis was applied to reconstruct elemental distributions in films and showed a nitridization depth of ~4nm for SiON and below 2nm for HfON. These results were compared with activation enthalpy for nitridization for different systems.

10:40am **AS-ThM8 Development of Reference Thin Films for Gate Oxide Thickness Determination and Ultra Shallow Junction Profiling, *D.W. Moon,*** KRISS, Korea **INVITED**

With the continued scaling down of CMOS devices beyond 50 nm, accurate and precise measurements of gate dielectric layer thickness and dopant profiles in ultra shallow junctions are no more simple and straightforward even with sophisticated techniques. In this presentation, the current status and remaining issues in analytical methodology for gate oxides and ultra shallow junctions are summarized and discussed. For accurate measurement of nm gate oxides thickness with sub atomic layer thickness precision, the thickness that each technique generates can be different and the difference should be understood in a complementary nature. Compared and discussed are the differences between high resolution transmission electron microscopy, grazing incidence X-ray reflectivity, medium energy ion scattering spectrometry, X-ray photoelectron spectroscopy, ellipsometry for accurate and precise determination of gate oxides down to sub nm thickness. For ultra shallow junction depth profiling, details of the sputtering processes in low energy secondary ion mass spectrometry are investigated regarding to the damage profiles and surface transient sputtering effect. Development of multiple delta layer reference thin films for ultra shallow junction profiling is reported on the growth and the application for sputtering rate calibration including the surface transient effect. Relevant activities of ISO TC 201 Surface Chemical Analysis and CCQM Surface and Micro/Nano Analysis WG and the present status and issues of reference thin films for gate oxide thickness determination and ultra shallow junction profiling will be briefly discussed.

11:20am **AS-ThM10 XPS and SIMS Analysis of HfSiON Films, *S. Miwa,*** *S. Kusanagi, Y. Murakami, H. Kobayashi,* Sony EMCS Corp., Japan

Nitrided Hafnium-silicate (HfSiON) is one of the promising materials for high-k gate dielectrics in advanced CMOS LSI. This material is so new that we have to investigate not only its electrical performance but also its chemical and physical properties. X-ray Photoelectron Spectroscopy (XPS) is the conventional technique for analyzing the chemical composition of thin films. We have found that XPS can also confirm the presence of phase separation in HfSiON films from the peak shift of the O1s signal. Secondary Ion Mass spectrometry (SIMS) is the most frequently used method to detect impurities in thin films and semiconductor substrates. In the case of high-k films grown by atomic-layer deposition or metal-organic chemical vapor deposition, it is necessary to use SIMS to determine whether H or C from precursor has been incorporated. SIMS can also be used N distribution in HfSiON films. However, it is difficult for conventional SIMS to observe the diffusion of Hf from HfSiON film to the Si substrate. Hf is moved from the film to the Si substrate by the probe ion beam, so we have employed backside-SIMS to observe Hf diffusion and obtain the precise Hf distribution near the HfSiON/Si interface.

11:40am **AS-ThM11 Nitridation of Hf Silicate Layers for Advanced CMOS Gate Oxides : A Core Level and Valence Band Study by Photoelectron Spectroscopy, *O. Renault,*** CEA-DRT-LETI, France*; N. Barrett, F. Calvat,* CEA-DSM-DRECAM, France*; Y. Le Tiec,* CEA-DRT-LETI, France*; P. Besson,* ST-Microelectronics, France*; F. Martin,* CEA-DRT-LETI, France

The nitridation of high-k materials is widely investigated for sub-65nm CMOS technology nodes@footnote 1@.In this contribution, we will present recent results of a core-level and valence band study by photoelectron spectroscopy, using both synchrotron and AlKa radiation, of nitrided Hf-silicate films for advanced gate oxides. Hf-silicate layers (3.5 nm-thick) were grown onto thin oxidized Si surfaces and then nitrided in an NH3 ambient. The valence band study at 80 eV photon energy reveals the introduction, upon nitridation, of localized N2p electronic states in the band gap of the silicate, thus confirming recent theoretical predictions@footnote 2@. The core-level analysis (Hf4f, N1s, Si2p) of as-grown, partially and totally etched silicate layers indicates that nitridation creates Hf-N bonds with a gradient from the surface to the interface depending on the nitridation temperature. Spectra recorded using synchrotron radiation with enhanced surface sensitivity and photon energy tunability will be presented and highlighted emphasizing the possibility to isolate the Si bonding states from the silicate layer itself. @FootnoteText@ @footnote 1@ M. Koike et al., extended abstracts, IEDM, 107 (2003).@footnote 2@ G. Shang, P. W. Peacock, J. Robertson, Appl. Phys. Lett. 84, 106 (2004).

Biomaterial Interfaces

Room 210D - Session BI+AS+SE-ThM

Surface Modification of Biomaterials

Moderator: D.G. Castner, University of Washington

8:20am **BI+AS+SE-ThM1 Strategies for the Biofunctionalization of Surfaces using Functional Polymer Layers, *J. Ruehe,*** University of Freiburg, Germany **INVITED**

The modification of surfaces with polymers for the promotion of cell outgrowth either in a dense layer or following a distinct pre-determined pattern is a challenging field of research with possible applications in the field of medical implants as well as for specific sensor devices. We present results from various studies in our group that range from the modification of bioimplant surfaces (e.g. glutar aldehyde treated porcine heart valves) with polymer monolayers in order to allow for a re-endothelialization of these devices to the arrangement of neuronal cells on a substrate by depositing synthetic and natural polymers on these chips in the form of a microarray. We will put a strong emphasis on synthetic approaches for establishing a strong, i.e. usually covalent interaction between the polymeric coating and the substrate in order to guarantee a sufficient long-term stability of the layer assemblies. These assemblies may be polymer monolayers as well as networks and we will also report on strategies for the incorporation of biological functions such as cell adhesion motifs or peptides. Finally, approaches for the laterally patterned deposition of these layers will be discussed.

9:00am **BI+AS+SE-ThM3 Interfacial Biomaterials: Guiding Biology on Synthetic Surfaces,** *E.B. Walsh, X. Huang,* Duke University*; M.W. Grinstaff,* Boston University*; **D.J. Kenan,*** Duke University Medical Center **INVITED**

Interfacial biomaterials represent a novel coating technology capable of directing biological processes at the interface between a biologic and a synthetic surface. The approach relies on screening combinatorial libraries to identify unique peptides that adhere to a synthetic target such as a plastic or metal, or to a biological target such as a protein or cell. Next, two or more adhesion peptides are synthetically coupled to create an interfacial biomaterial that mediates the interaction of the protein or cell with the synthetic material. Other interfacial biomaterials may be created by coupling known signaling molecules to peptides that bind synthetic materials. Mixtures of interfacial biomaterials may be applied to a surface to achieve a particular desired biological outcome, such as adhesion of a given cell type to the surface, followed by induction of one or more signal transduction pathways. These interfacial biomaterials are amenable to numerous coating and patterning techniques suggesting their use for diverse applications ranging from biomedical device coatings to anti-infectives to tissue engineering.

9:40am **BI+AS+SE-ThM5 Antibacterial Surfaces of Covalently Immobilized Dendrimers,** *D. Weber, N.R. Choudhury,* University of South Australia*; **H.J. Griesser,*** University of South Australia, Australia

The need to limit bacterial adhesion to surfaces of biomedical implants, contact lenses, and other devices has prompted considerable recent research into antibacterial compounds and coatings. To ensure long-term efficacy and eliminate concerns about potential adverse biological effects on sensitive organs remote from the implant site, release strategies seem less suitable, and the covalent surface immobilization of antibacterial compounds is the approach of choice in our work. However, the question then becomes whether a covalently immobilized antibacterial is still biologically active, and can maintain activity over extended service life spans. In this study we have principally explored the surface immobilization of dendrimers, which have previously been shown to be antibacterially active in solution (eg CZ Chen and SL Cooper, Biomaterials 23 3359 2002). Another approach involves extracts of some Australian plant species, but their chemical characterization and synthesis is less developed. We have immobilized amine-terminated dendrimers onto aldehyde plasma polymer interlayers via reductive amination and characterized the coatings by XPS, ToF-SIMS, and AFM. Using various plasma conditions the surface density of aldehyde groups can be varied. The surface density of immobilized dendrimers is determined from XPS elemental ratios, using the dendrimer-specific N signal. Following surface immobilization, the remaining amine groups are quaternized in order to produce a cationic surface. The distinct signal arising from quaternary N in the XPS N 1s spectrum enables assessment of this reaction. The plasma approach also enables us to apply this coating strategy onto a wide variety of substrates both polymeric and inorganic (ceramic and metallic).

10:00am **BI+AS+SE-ThM6 Biomimetic Vascular Engineering: Exploiting Concepts from Nature to Create New Biomaterial Interfaces**, ***R.E. Marchant***, Case Western Reserve University **INVITED**

The abundance of complex supramolecular structures in Nature provides lessons in structural hierarchy and functional efficiency that are being explored and exploited in the development of novel biomimetic strategies for creating new biomaterial interfaces for biomedical applications. Mimicking and adapting structural concepts from Nature to create tissue compatible interfaces for biomaterials that incorporate molecular recognition and self-assembly will be the central theme of this presentation. We have developed a biomaterial architecture using "surfactant polymers" that undergo surface and self-induced assembly on hydrophobic surfaces. Our biomimetic designs benefit from understanding the structural and functional properties of the corresponding system in Nature. One example is the external region of a cell membrane, known as the glycocalyx, which is dominated by a complex milieu of glycosylated molecules. The glycosylated molecules direct specific interactions such as cell-cell recognition, and provide an important physical basis for maximizing steric repulsion that prevents undesirable non-specific cell and molecular adhesions. Conversely, understanding the nature of a cellâ?Ts adhesive interactions with the extracellular matrix facilitates design of biomimetic materials with cell adhesion properties. Using these biomimetic concepts, we have designed and studied oligosaccharide and peptide surfactant polymers that provide suppression of non-specific protein interactions and facilitate well-controlled interactions with endothelial cells.

10:40am **BI+AS+SE-ThM8 Stability of Polypeptide Multilayers as Studied by in situ Ellipsometry: Effects of Drying and Post-Buildup Changes in Temperature and pH**, *T.J. Halthur,* YKI AB, Institute for Surface Chemistry, Sweden; *P. Claesson,* KTH, Royal Institute of Technology, Sweden; ***U. Elofsson***, YKI AB, Institute for Surface Chemistry, Sweden

Polyelectrolyte Multilayers (PEM) of poly(L-glutamic acid) (PGA) and poly(L-lysine) (PLL) with a initial layer of polyethyleneimine (PEI) were built on silica and titanium surfaces using the Layer-by-Layer (LbL) technique. The stability of the film during drying/rewetting, temperature cycles and pH shifts was studied in situ by means of ellipsometry. The filmthickness was found to decrease significantly (approximately 70%) upon drying, but the original film-thickness was regained upon rewetting and the buildup could be continued. The dry thickness was found to be extremely sensitive to ambient humidity, needing several hours to equilibrate. Changes in temperature and pH was also found to influence the multilayer thickness, leading to swelling and de-swelling of as much as 8% and 10-20% respectively. The film does not necessarily regain its original thickness as the pH is shifted back, but instead shows clear signs of hysteresis.

11:00am **BI+AS+SE-ThM9 PCA of TOF-SIMS Spectra from p(AAm-co-EG/AAc) IPNS on Quartz**, ***D.J. Graham***, University of Washington; *G.M. Harbers, K.E. Healy,* University of California, Berkeley; *D.G. Castner,* University of Washington

PCA of TOF-SIMS has been carried out on many well defined model surfaces in structured experiments. These studies have shown the utility of PCA in extracting information from TOF-SIMS experiments from a wide variety of substrate surfaces. This work reports on the application of PCA to a more complex interpenetrating polymer network system. The goal of this project was to verify each step in the IPN synthesis procedure on a quartz substrate. This system presents a challenge to PCA due to the similarity of the polymers used in the IPN and the addition of a peptide chain. PCA of the entire data set (including all synthesis steps for the IPN) showed that PC1 was able to separate most samples. The PC1 loadings were dominated by the overall differences between the hydrocarbons on the bare quartz and the PEG related peak fragments after the addition of the IPN onto the quartz surface. This is likely due to the high PEG content of the IPN polymers. PCA comparing each successive synthesis step gave further insight into the success of the IPN chemistry. PCA was able to distinguish each surface modification up until the addition of the peptide precursor and peptide. The presence of the peptide was verified in subsequent experiments where it was shown that RGD-peptide modified p(AAm-co-EG/AAc) surfaces supported rat calvarial osteoblast adhesion, proliferation, and matrix mineralization. Consequently,surfaces without the RGD peptide or with a control RGE peptide did not support cell attachment. PCA also gave insight into the uniformity of the surface modifications by way of the scores plots. Increasing scatter was seen in the last few synthesis steps suggesting that a less uniform surface chemistry was achieved. The trends seen in the PCA of the TOF-SIMS data were consistent with those seen by XPS.

11:20am **BI+AS+SE-ThM10 Development of an Antimicrobial Polymer Surface Coating for the Prevention of Staphylococcal Infections**, ***M. Anderle***, *L. Pasquardini, L. Lunelli, R. Canteri, P. Villani, C. Pederzolli,* ITC-irst, Italy

The proliferation of pathogenic microorganisms on polymer surfaces is one of the most widespread causes of failure of biomedical devices such as catheters, medical implants, vascular graft and joint prostheses. The inhibition of pathogenesis and subsequent mechanisms of protection are possible by killing bacteria in the first steps of colonization. This work describes a polymeric surface coating with liposomes as method to provide a sustained delivery of antibiotics into the local micro-environment of the implant. In this study liposome formulations composed of Phosphatidylcholine (PC), Distearoyl-sn-Glycero-3-Phosphoethanolamine-N-MethoxyPolyethylene glycol (DSPE-PEG) and cholesterol are utilized. Liposomes, different in size, are attached to an amine activated substrate through the formation of covalent bonds with the distal end of the PEG (Polyethylene glycol) derivative molecules. Data on the surface coating using large unilamellar vesicles (LUV) and multilamellar vesicles (MLV) will be shown. The AFM analysis is performed to study the nanoscale structure of the coated surface while the fluorescence spectroscopy and microscopy are engaged to determine the immobilisation efficacy adding a fluorescent lipid (L-@alpha@-Phosphatidylethanolamine-N-lissamine rhodamine B sulfonyl) to the liposome composition. The MLV coating on polystyrene shows a more uniform distribution with a lipid concentration of about 2x10@super 15@ mol/cm@super 2@. Finally drug (rifampicin) release and bacterial colonisation rates with their correlation will be reported.

11:40am **BI+AS+SE-ThM11 Spectroscopic Characterization of Surface-Immobilized Antibacterial Furanone Coatings**, ***S. Al-Bataineh***, *H.J. Griesser,* University of South Australia, Australia; *M. Willcox,* University of New South Wales, Australia; *L.G. Britcher,* University of South Australia, Australia

The colonisation by bacteria of biomedical devices presents a serious concern for human implant surgery. In this study, we explore how bacterial colonisation can be prevented by the appropriate design and fabrication of antibacterial coatings, with a major focus on surface-immobilised furanone molecules. These compounds are produced naturally by the marine algae, Delisea pulchra and are used as defence agents to prevent fouling on their surface@footnote 1@. Several studies have shown that brominated furanones as well as synthetic analogues possess potent antimicrobial activity against bacteria@footnote 2@@super ,@@footnote 3@. The previously used azide protocol was adopted to prepare furanone coatings@footnote 4@. XPS and ToF-SIMS results showed successful surface modifications and furanone immobilisation. Detailed analysis of the C 1s and N 1s XPS spectra using constrained curve fitting showed that they are more complicated than anticipated from the theoretical reaction scheme. In addition, the presence of a Br@super-@ peak partially overlapped with a C-Br peak indicated that furanones are partially degraded on UV illumination. More surface characterisations are needed for full understanding of the chemical reactions that occurred. Seven furanone compounds used in this study were tested for their ability to inhibit biofilm formation and growth of two bacterial strains, Staphylococcus aureus (Saur19) and Pseudomonas aeruginosa (Paur6206). Initial results are promising; detailed investigation of the efficacy of the coatings is ongoing. Furthermore, none of the compounds used in this study showed any cytotoxicity potential at the tested concentrations. @FootnoteText@ @footnote 1@ de Nys R. et al., 1995, 4:259-71.@footnote 2@ Kjelleberg S. et al., Patent No. PCT/AU99/00284, 1999.@footnote 3@ Read R. et al. PCT international application PQ6812, 2001.@footnote 4@ Muir B. et al., Proc. 6th World Biomat. Congr., Hawaii, May 2000, p. 596.

Magnetic Interfaces and Nanostructures
Room 304A - Session MI-ThM

Magnetic Oxides and Half-Metallics

Moderator: G.D. Waddill, University of Missouri-Rolla

8:20am **MI-ThM1 Defect Mediated Ferromagnetic Coupling Through an Insulating Barrier Layer@footnote 1@**, ***P.A. Dowben***, University of Nebraska; *R.-H. Cheng,* Argonne National Laboratory; *B. Doudin,* University of Nebraska **INVITED**

Interlayer exchange coupling between two ferromagnetic films, separated by a nonmagnetic non metallic spacer (semiconductor and insulator spacer materials) does occur. This coupling sometimes appears to be distinct from the very low temperature tunneling phenomena between two ferromagnets, through a dielectric spacer layer, as the coupling is sometimes oscillatory. The ferromagnetic coupling between Co and CrO@sub2@, through an insulator (Cr@sub2@O@sub3@) may be rel ated to defect states in the insulating barrier layer.@footnote 2@ In the native Cr@sub2@O@sub3@ surface layer, it appears that at low temperature the conduction band edge electrons are trapped or immobile, and at high temperature there is greater mobili ty. Combined photoemission and inverse photoemission temperature dependent studies confirm the occurrence of a defect mediated blockade energy. It may well be that many defect states are spin polarized, possibly by proximity to the ferromagnetic interface. Other complications exist. The interpretation of junction magneto-resistance results must now assume that ferromagnetic metals will NOT generally form abrupt interfaces with transition metal oxide dielectric barriers. It must be recognized that many met al to metal oxide interfaces involve further oxidation and reduction making such interfaces very heterogeneous, so that nominal CrO@sub2@/Cr@sub2@O@sub3@/Co magnetic junctions are, in fact, more complex multilayers systems akin to a CrO@sub2@/Cr@sub2@O@sub3@/CoO/Co system. @FootnoteText@@footnote 1@ The support of the Office of Naval Research, and the NSF MRSEC (DMR 0213808) are gratefully acknowledged. The authors would like to acknowledge a number of helpful conversations with E. Tsymbal.@footnote 2@ Ruihua Cheng, A.N. Caruso, L. Yuan, S.-H. Liou, and P.A. Dowben, Applied Physics Letters 82 (2003) 1443-1445 .

9:00am **MI-ThM3 Measuring Spin Polarization at the Fermi Level in Potential Half-Metallic Ferro-magnets***,* ***J.G. Tobin,*** Lawrence Livermore National Laboratory*; T. Komesu, G.D. Waddill,* University of Missouri-Rolla

We have utilized synchrotron-radiation-based techniques to investigate possibly half-metallic ferromagnetic (HMFM) materials. HMFM'Ts are, of course, potential sources of pure spin polarized electrons for spintronic and magnetic information storage devices. These investigations include the application of spin-resolved photoelectron spectroscopy (SPES) to systems such as Fe3O4@footnote 1@ and X-ray Absorption Spectroscopy (XAS) to Zintl compounds such as Yb14MnSb11. @footnote 2@ In the case of Fe3O4, despite having performed the studies at the relatively high photon energy of 160 eV, significant problems with residual surface effects were observed. In order to circumvent or at least minimize these surface complications and to get a better measure of the true bulk spin polarization, we have moved our spin-resolving spectrometer@footnote 3@ to Beamline 4 at the Advanced Photon Source,@footnote 4@ where an Elliptically Polarizing Undulator (EPU) can provide high brightness radiation in the range of 500 eV to 3000 eV. Our first spin-resolved results of the Fe2p core levels@footnote 5@ have confirmed the feasibility of these experiments. Plans for the interrogation of potential half-metallic ferromagnets such as GaMnAs and related materials at these higher energies will be discussed. @FootnoteText@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. @footnote 1@ S.A. Morton, G.D. Waddill, S. Kim, I.K. Schuller, S.A. Chambers, and J.G. Tobin, Surface Science Letters 513, L451 (2002). @footnote 2@ A.P. Holm, S.M. Kauzlarich, S.A. Morton, G.D. Waddill, W.E. Pickett, and J.G. Tobin, J. Amer. Chem. Soc. 124, 9894 (2002). @footnote 3@ M. Hochstrasser, J.G. Tobin, E. Rotenberg and S.D. Kevan, "Spin-Resolved Photoemission of Surface States of W(110)-(1X1)H," Phys. Rev. Lett. 89, 216802 (2002). @footnote 4@ J.W. Freeland et al, Rev. Sci. Instrum. 73, 1408 (2002). @footnote 5@ http://www-cms.llnl.gov/s-t/aps.html

9:20am **MI-ThM4 Transition Metal Oxides in Reduced Dimensions***,* ***J. Shen,*** Oak Ridge National Laboratory **INVITED**

When the spatial dimension of a material becomes comparable or even smaller than the characteristic length scale of the relevant cooperative phenomena, it is expected that all related physical properties including phase transitions of this material will be dramatically changed. In this work, we focus on the discovery, understanding, and design of low-dimensional 3d transition metal oxides (TMO). We use both physical and chemical methods including laser MBE growth, hydrothermal synthesis, and nanoparticle-catalyzed processes to grow TMO thin films and nanowires. The electronic and magnetic properties of the TMO thin films have been investigated by in-situ scanning tunneling microscopy and ex-situ SQUID magnetometer. We have observed both large-scale (over a few tens nanometers) and nano-scale electronic phase separation (PS) in epitaxially grown thin films of (La5/8-0.3Pr0.3)Ca3/8MnO3. While the large PS domains are present only below the Curie temperature, the nano-scale PS clusters exist at temperatures both below and above Curie temperature. The latter implies that the small PS may originate from doping-related disorder. The TMO nanowires of doped manganites are single crystals with tunable diameters. SQUID magnetometer and e-beam lithography prepared four-point probes have been used to study their magnetic and transport properties.

10:00am **MI-ThM6 Growth and Characterization of PLD Grown Co Doped TiO@sub 2@***,* ***S.T. Prisbrey,*** UC Davis, Lawrence Livermore National Laboratory*; S.P. Vernon,* Lawrence Livermore National Laboratory

14-20 nm thick 3.7%Co doped TiO@sub 2@ and 5.4% Co doped TiO@sub 2@ have been grown by PLD on LaAlO@sub 3@ (100) substrates. @theta@-2@theta@ x-ray diffraction scans suggest that the films are crystalline and oriented with the z-axis perpendicular to the film surface. AFM/MFM scans show the film to be smooth but with a high defect density (~10@super 6@/cm@super 2@). Defects on the surface of the film do have a magnetic response. X-ray absorption spectroscopy with CoTiO@sub 3@, CoO, and Co@sub 3@O@sub 4@ shows the cobalt to be in the Co@super +2@ formal oxidation state in the majority of the films grown but with no discernable correlation between known deposition parameters and the formal oxidation state of the Co. SQUID magnetic measurements and VSM measurements show that the films are magnetic at room temperature with T@sub c@ > 340°C. Surface ion mass spectrometry was employed to determine that the actual cobalt concentrations in the films are the same as those of the target. Samples were cooled in a field and B-H loops were measured to determine if the magnetic interaction is similar to that of a spin glass.

10:20am **MI-ThM7 Room-Temperature Ferromagnetism in Cr-doped TiO@sub 2@ Anatase***, T.C. Droubay, S.M. Heald, S.V. Shutthanandan, S.T. Thevuthasan,* ***S.A. Chambers,*** Pacific Northwest National Laboratory*; J. Osterwalder,* Physik-Institut der Universitat Zurich, Switzerland

Since the initial discovery in 2001, the possibility of ferromagnetism in doped oxide semiconductors has spawned a flurry of research activity around the world. Among the new materials that have been investigated, Co-doped TiO@sub 2@ anatase has garnered much attention due to its ferromagnetic response, which persists well above room temperature. Reports of doping TiO@sub 2@ anatase with other magnetic transition elements, however, are scarce. We have carried out a detailed study of the growth and properties of epitaxial Cr-doped TiO@sub 2@ anatase on LaAlO@sub 3@ (001) using oxygen-plasma assisted molecular beam epitaxy. These films are found to be single-phase and homogenous, with Cr uniformly substituting for Ti in the lattice. Cr K-shell x-ray absorption near-edge spectroscopy shows that the formal oxidation state of Cr is +3 throughout the films, with no evidence for either elemental Cr or half-metallic CrO@sub 2@. These films are insulating as grown, yet exhibit room temperature ferromagnetism aligned in-plane with a saturation magnetization of ~0.6 Bohr magnetons per Cr atom. Introduction of free electrons by incorporation of additional oxygen vacancies via post-growth annealing in UHV increases both the n-type conductivity and the saturation magnetization, without deleterious effects on the homogeneity or crystallinity of the films. None of the existing models of magnetism in semiconductors can explain ferromagnetism in the absence of free carriers for a dilute system. We will present a novel exchange mechanism to do so.

10:40am **MI-ThM8 Synthesis of Room-Temperature Ferromagnetic Materials by Ion Implantation: Transition-Metals-Doped TiO@sub 2@ (110) Rutile***,* ***V. Shutthanandan,*** *S.T. Thevuthasan, S.M. Heald, T.C. Droubay, M.H. Engelhard, C.M. Wang, D.E. McCready, T.C. Kaspar, S.A. Chambers,* Pacific Northwest National Laboratory*; P. Nachimuthu, B.S. Mun,* Lawrence Berkeley National Laboratory

There is growing interest in diluted magnetic semiconductors (DMS) in the emerging field of spintronics. It has recently been demonstrated that certain oxide semiconductors doped with magnetic transition metal elements show room-temperature ferromagnetism. In particular, titanium dioxide in both anatase and rutile phases appear to be among the most promising oxide semiconductors for DMS applications. In this study, we show that ferromagnetic transition metal doped TiO@sub 2@ (110) rutile single crystals can be successfully synthesized using ion implantation by carefully controlling implantation parameters such as temperature and ion fluence. Co, Cr, Ni and Fe ions with 100 keV energy were implanted at 875 K to 1075 K and an ion fluence of ~1.25x10@super 16@ ions/cm@super 2@. Vibrating sample magnetometer (VSM) measurements clearly show room temperature ferromagnetic responses with magnetic moments ranging from 0.30 to 0.70 µ @sub B@ /atom. X-ray photoelectron spectroscopy (XPS) depth profiling and Rutherford backscattering spectrometry (RBS) measurements reveal that most of the implanted dopants are uniformly distributed to a depth of ~300 nm with an average concentration of ~1 to 3 at%. K-edge x-ray absorption near edge spectra (XANES) obtained from the implants show that all of the implanted atoms are oxidized and that the formal oxidation is +2 for Co and Ni, +3 for Cr and a mixture of +2 and +3 for Fe. There is no evidence that the dopant is in the metallic state in these implanted samples. In addition, surface-sensitive total electron yield (TEY) and bulk-sensitive total florescence yield (TFY) obtained from the L-edge of Ti and implants and K-edge of O demonstrate that the structural environments in both surface and bulk regions of rutile TiO@sub 2@ are not significantly affected by the incorporation of implanted species.

11:00am **MI-ThM9 MBE Growth and Room Temperature Ferromagnetism in Epitaxial Co-doped SrTiO@sub 3@***, **T.C. Kaspar**, T.C. Droubay, S.M. Heald, C.M. Wang, V. Shutthanandan, S.T. Thevuthasan, S.A. Chambers,* Pacific Northwest National Laboratory

Room temperature ferromagnetism in dilute magnetic semiconductors (DMSs) is highly desirable for practical spintronic devices. The observation of room temperature ferromagnetic behavior in doped wide bandgap semiconducting oxides such as Co-doped ZnO, Mn-doped ZnO, and Co-doped anatase and rutile TiO@sub 2@ has raised the possibility of DMS behavior in other oxide systems. Work on these materials has also revealed the critical importance of thorough materials characterization to rule out ferromagnetic contributions from metallic clusters or other secondary phases. Recently, Co-doped La@sub 0.5@Sr@sub 0.5@TiO@sub 3@ was found to exhibit ferromagnetic behavior at room temperature.@footnote 1@ In the present study, epitaxial SrTi@sub 1-x@Co@sub x@O@sub 3@ thin films (0 < x < 0.15) have been deposited on SrTiO@sub 3@(001) substrates by oxygen-plasma-assisted molecular beam epitaxy (OPAMBE). Smooth films free of surface particles or clusters are obtained. As-deposited films are insulating (@rho@ > 5 k@Omega@-cm); however, room temperature ferromagnetism is observed for < 5% Co doping, with a high magnetic moment and 10-25% remanence. Films doped at higher concentrations (> 5%) do not exhibit ferromagnetism. Thorough materials characterization was employed, including XPS for film composition, AFM and TEM to observe film morphology and the possible inclusion of secondary phases, and RBS and PIXE to determine the precise Co concentrations. A comprehensive study of Co K-edge XANES and EXAFS data to determine details of the Co charge state and local environment was also carried out. F-center mediated exchange will be discussed as the possible mechanism of ferromagnetic ordering in Co:STO. In addition, preliminary results of epitaxial SrTi@sub 1-x@Co@sub x@O@sub 3@ growth on Si(001) will be presented, and the differences in deposition on oxide and semiconductor substrates will be discussed. @FootnoteText@ @footnote 1@ Zhao, Y.G., et al. Appl. Phys. Lett. 83, 2201 (2003).

11:20am **MI-ThM10 Characterization of Transition Metal Doped ZnO Films and Nanostructures***, **D.H. Hill**, L. Wielunski,* Rutgers University*; D.A. Arena,* Brookhaven National Lab*; R. Bartynski, P. Wu, Y. Lu,* Rutgers University

A crucial element for the success of spintronics is finding a material that combines the desirable properties of ferromagnets and semiconductors. Diluted magnetic semiconductors (DMS) are intriguing materials that offer the possibility of studying magnetic phenomena in crystals with a simple band structure and excellent magneto-optical and transport properties. ZnO, a wide bandgap (~3.3 eV) semiconductor that has received increasing attention due to its broad applications and its many desirable material properties, has recently has been identified as a promising DMS candidate for room temperature spintronics. We have characterized the chemical, compositional, and magnetic properties of TM-doped ZnO films grown by MOCVD and sputter deposition on a variety of substrates. Doping with Mn, and Fe by either diffusion, co-sputtering, or ion implantation has been investigated, and each doping method results in very different dopant depth profiles as revealed by Rutherford backscattering spectrometry. Soft x-ray absorption spectroscopy (SXAS) indicates that the TM dopant may be in either the 2+ or 3+ oxidation state and depends upon doping method. Furthermore, the XAS results are consistent with the TM ions being substitutional for Zn. Squid magnetometry shows that some doping methods yield films exhibiting ferromagnetic behavior, with some Fe-doped films having the Curie temperatures above room temperature. Finally, we discuss the properties of MOCVD-grown ZnO nanotips that have been doped by TM ion implantation.

11:40am **MI-ThM11 Effects of Heat Treatment on the Magnetic Properties of Nickel Cobalt Oxide Films***, **R.R. Owings**, G.J. Exarhos, T.C. Droubay, C.F. Windisch,* Pacific Northwest National Laboratory

Spinel films of reactively sputtered nickel cobalt oxide exhibit an increase in saturation magnetization, up to ~5x, when rapidly quenched following heat treatment at 375° C for 10 minutes in air. The films appear to be weakly ferromagnetic with an in-plane saturation occurring in a field greater than 2000 G. Heat treatment followed by rapid quenching has also been shown to increase conductivity. Although the exact mechanism that relates the conductivity to the saturation magnetization is not well understood, the results of this work suggest that there is a relationship between the carrier movement and the spin orientation of the occupied orbitals in the octahedral or tetrahedral lattice positions. The effects of the heat treatment and cooling rate on the magnetic moment, electrical conductivity, index of refraction, IR transmission, and cation disorder are also discussed.

Manufacturing Science and Technology
Room 303B - Session MS-ThM

Advanced Process Control

Moderator: B. Van Eck, Sematech

8:40am **MS-ThM2 Fault Detection and Classification Using RGA in Semiconductor Manufacturing***, Y. Xu, J. Byrne, H. Clark, J. Parker,* IBM*; **J. Blessing**,* MKS

A new advanced residual gas analysis (RGA) system was jointly developed by IBM and MKS-Spectra and implemented in IBM's 300-mm wafer fabrication facility for the purpose of process monitoring and fault detection. The RGA system was integrated into the Computer Integrated Manufacturing (CIM) architecture using IBM's Advanced Process Control (APC) third party interface, an Extensible Markup Language (XML) based messaging system. The APC third party interface presents a brand new APC/sensor integration methodology allowing the RGA application (or any other sensor for this matter) to have access to both tool level event/trace/recipe data and fab level process/wafer information. A centralized database is used to manage the RGA system and to store summarized RGA data. Several examples will be offered to demonstrate how the role of the RGA system has expanded far beyond traditional photoresist detection and tool vacuum integrity. Its ability to quickly detect the undesirable process variations and incoming contaminations (photoresist or non-photoresist) proves to be critical to improving product yield, tool availability and ultimately the profitability of the fab. RGA fault classification is another important topic that will be covered. This classification is required to facilitate the proper handling of various RGA faults. One approach under consideration is to apply multi-variable analysis techniques to RGA data analysis. Some preliminary results will be given in the discussion.

9:00am **MS-ThM3 Using Process Control to Address Manufacturing Challenges at 300mm***, T.J. Sonderman, **C. Bode**,* AMD **INVITED**

The implementation of fully automated fab technologies will help ease the transition to 300mm manufacturing by making the most of the 300mm toolset capabilities. The transition to 300mm necessitates a level of process control improvement commensurate with the increase in the intrinsic value of the processed wafers. The key will be to keep these costs low while maximizing the value of each wafer. Part of the solution lies in establishing a fully automated system that allows for maximum predictability of output with manufacturing capabilities such as Advanced Process Control (APC). APC, a part of AMD’s Automated Precision Manufacturing (APM) technology, will be one of the key manufacturing technology that supports the transition. APC capabilities will need to evolve past lot-to-lot control to wafer-to-wafer control. 300mm tools will need to consider wafer-to-wafer control and extend the ability to change the process recipe for each individual wafer, in an automated fashion, as required. In addition, the control of individual processes will need to be integrated into a more holistic approach. This presentation will explore the evolution from unit process control to fab-wide automation. A holistic approach for factory automation goes beyond the optimization of performance within a given process or batch of wafers to focus on optimizing the output of the entire factory. The systems enabling optimization of process control are developed in coordination with advanced systems for automated yield analysis and production control. This integrated approach allows for a process control system that is both more flexible and more precise. Thomas Sonderman will discuss the manufacturing challenges that organizations face within 300mm and the benefits afforded to the market by moving to full automation. His presentation will draw on years of experience in the integration of these technologies to describe the essentials of a highly-automated 300mm manufacturing facility.

9:40am **MS-ThM5 Run-to-Run Process Control And Equipment Monitoring for Advanced Etch Applications.***, **J. Yamartino**, D. Mui, H. Sasano, W. Liu, M. Shen, J.P. Holland, V. Todorow, A.M. Paterson,* Applied Materials, Inc.

Run-to-run process control provides a means for significantly improving the process capability index of a process tool as well reducing cycle time of product wafers. The Applied Centura Transforma Etch system provides the capability for controlling and reducing wafer-to-wafer CD variations for critical etch processes including gate etch. These capabilities includes the ability to adjust multiple process parameters based on multiple inputs from either the Fab Host or integrated CD metrology for both feedforward and feedback applications. In addition, an analysis of etch chamber data from several Applied Materials Etch systems demonstrates the importance of monitoring the chamber data for stability and excursion control. A model of the chamber behavior is created using a multivariate analysis of chamber data taken under known good production conditions. This model is then used as a baseline to which subsequent runs are compared. Excursions are detected using an overall health index and classified in terms of the chamber variable or variables responsible for the excursion. The run-to-run monitoring functionality provides a powerful means for maintaining equipment uptime and reducing wafer scrap. Finally, run-to-run monitoring of chambers which are under feedforward/feedback control enhances the capabilities of advanced process control. Examples from production data demonstrate the important link between monitoring and control.

10:00am **MS-ThM6 Gate Sidewall Profile Control for Plasma Etch Tool***, **J. Tanaka**,* Hitachi Ltd., Japan*; A. Kagoshima, D. Shiraishi, H. Yamamoto, S. Ikuhara, M. Yoshigai,* Hitachi High Technologies Corporation, Japan

The scale of semiconductor devices has been shrinking year by year. Plasma etch tools have to meet demands for the tight control of gate critical dimensions (CD) for complementary metal oxide silicon (CMOS) devices. Although the hardware of plasma etch tools has been modified to stabilize the gate CD after the etch process, there remains slight wafer-to-wafer drift of the gate CD caused by the changing wall surface conditions. Run-to-run feedback control of the etch process is beginning to be used to eliminate the residual gate CD drift. To eliminate the gate CD drift by run-to-run control, we controlled the oxygen flow rate. Then we found the gate CD could not be controlled without changing the gate sidewall profile. To monitor the gate sidewall profile we used a CD scanning electron microscope (CDSEM). The CDSEM can measure a line width from the intensity profile of secondary electron. Thus it is natural that we should expect the intensity profile measured by the CDSEM to have a strong correlation with gate profile. We found the change in the gate sidewall profile can be monitored using the intensity profile of CDSEM. The etch process used for the experiment consists of four steps: a breakthrough step, a main etch step 1 (ME1), a main etch step 2 (ME2), and an over etch step. In our first trial experiment we controlled oxygen flow rate in ME2. Although the gate CD changed as expected, the gate sidewall was tapered to degrade its vertical shape. Thus we moved the control step to ME1. When we changed the oxygen flow rate in ME1, we could control the gate CD without changing the gate sidewall profile. Finally a gate CD drift in a lot was suppressed keeping the same gate sidewall profile.

10:20am **MS-ThM7 DRAM Gate CD Control in Dry Etch Process using Optical Integrated Metrology***, **Y.J. Jung**, Y.J. Kim, G.J. Min, C.J. Kang, H.K. Cho, J.-T. Moon,* Samsung Electronics Co., LTD., Korea*; J.W. Shon,* Lam Research Corporation

In current CMOS technology, a traditional sequence to obtain a target post etch CD is to perform lithography patterning and measure the CD in resist followed by dry etch and strip process. There is a specification for the CD in resist, which may result in target post etch CD. After the measurement of the CD in resist by using in-line scanning electron microscope (SEM), it is determined whether the rework process of lithography is necessary or not to meet the specification of the CD in resist. This kind of traditional CD control sequence, however, may be a source of following problems. First, since the measurement of the CD in resist cannot be performed for every lot as well as every single wafer due to throughput in mass production environment, it is not sure that all lots and/or wafers meet the specification of the CD in resist. Second, rework process for out of specification requires additional time, resources, and cost, which result in the decrease of productivity. Third, the measurement of the CD in resist using SEM causes CD slimming, which may give uncertainty error in CD determination. Although CD control in dry etch process using the optical integrated metrology is one of the promising candidates to overcome the above problems, it has not been applied in the DRAM Gate etch process due to the difficulty in thick Si@sub 3@N@sub 4@ hard mask. In this work, DRAM gate CD control in dry etch process is applied to sub-100 nm transistor fabrication. Gate etch of Si@sub 3@N@sub 4@ hard mask is performed using dual-frequency capacitively coupled plasma (DF-CCP) type etcher. After the CD in resist for each wafer is measured using the optical integrated metrology, the process controller determines a proper process condition to meet the target post etch CD according to the predetermined model of CD control with the measured CD in resist. Throughout this CD control in DRAM gate etch process, the variation of CD in resist (@>=@10nm) is reduced dramatically (@<=@2nm).

10:40am **MS-ThM8 Improving Etch Process Control with Advances in Vacuum Measurement***, J. Sipka, **S. Pewsey**, D. Leet,* Mykrolis Corporation

As each successive technology node is developed, staying the course of 'Moore's Law' has required device size scaling, and often, new materials development as well as tighter manufacturing process control, adherence to specifications and improved, tighter tolerances for chamber level devices. Process pressure repeatability at low mTorr setpoints is critical in obtaining the desired yields in Etch Processes. The process chamber pressure control system is a key component in achieving the process repeatability. At the heart of the chamber pressure control system is the Capacitance Diaphragm Gauge (CDG). If the fundamental vacuum measurement shifts or varies over time, the chamber pressure control sub-system will track this, resulting in changes in etch rate resulting in wafer lot to lot variability. A study was conducted to correlate (Etch) Process CD data with the (zero) stability of a new generation of Digital Process Vacuum Gauges. This paper will show test results of long term zero stability, process repeatability, and environmental sensitivity of a low-pressure heated digital capacitance diaphragm gauge under typical Semiconductor Etch conditions and under controlled test conditions. This paper will also address the causes of zero output shifts on Capacitance Diaphragm Gauges and design techniques utilized to minimize this effect.

11:00am **MS-ThM9 New Intelligent Molecular Flow Sensor-Experimental Definition of Flow Properties***, **H.S. Sagi**,* ATC, Inc.

A new Intelligent Molecular Flow Sensor (IMFS) enables, for the first time, direct gas flow measurements in the transitional and molecular flow regimes, as well as in the slip and continuum flow regimes, thereby enabling flow measurements at pressures ranging from vacuum through atmospheric. The properties of this sensor are investigated, along with the sensor's transitional operating ranges. The IMFS operates as a mass flow sensor (directly measures the mass flow) in the transitional and molecular flow regimes, and it operates as a volumetric flow sensor in the continuum and slip flow regimes. Understanding of these properties and ranges of operation are critical for demanding leak testing, sealed closure integrity testing and vacuum test applications.

Nanometer-scale Science and Technology
Room 213C - Session NS1-ThM

Nanoscale Fabrication

Moderator: C.R.K. Marrian, IBM Almaden Research Center

8:20am **NS1-ThM1 Three-Dimensional Nanotechnology by Focused-Ion-Beam Chemical-Vapor-Deposition***, **S. Matsui**,* Himeji Institute of Technology, CREST-JST, Japan **INVITED**

The deposition rate of focused-ion-beam chemical-vapor-deposition (FIB-CVD) is much higher than that of electron-beam chemical-vapor-deposition (EB-CVD) due to factors such as the difference of mass between electron and ion. Furthermore, FIB-CVD has an advantage over EB-CVD in that it is more easily to make a complicated 3-dimensional nanostructures. Because, a smaller penetration-depth of ion compared to electron allows to make a complicated 3-dimensional nanostructures. For example, when we make a coil nanostructure with 100 nm linewidth, electrons with 10-50 keV pass the ring of coil and reach on the substrate because of large electron-range (over a few µm), so it is very difficult to make a coil nanostructure by EB-CVD. On the other hand, as ion range is less than a few ten-nm, ions stop inside the ring. Three-dimensional nanostructure fabrication using FIB-CVD has following advantages. (1) As a beam diameter of FIB is 5nm, 3 D nanostructures with a few ten nm can be fabricated by FIB. (2) 3D nanostructures made of metal, semiconductor, and insulator etc. can be fabricated by using various source gases. Three-dimensional nanotechnology using FIB can be widely applied to electronics, mechanics, optics, and biology. We have demonstrated the fabrication of free-space-nanowiring, electrostatic nano-actuator, bio-injector and electrostatic nano-manipulator by using FIB-CVD.

9:00am **NS1-ThM3 Integration of Ion Beams with Scanning Probes for Local Doping and Chemical Analysis of Materials***, T. Schenkel, A. Persaud,* E. O. Lawrence Berkeley National Laboratory*; I.W. Rangelow,* University Kassel, Germany*; S.J. Park, F.I. Allen,* E. O. Lawrence Berkeley National Laboratory*; K. Ivanova,* University Kassel, Germany

We describe our newly developed scanning probe instrument which integrates ion beams with imaging and alignment functions of a piezo resistive scanning probe in high vacuum. In the past, Scanning Probe functions have been combined successfully with lasers, excited reactants, as well as neutral beams for surface analysis or materials modification at a nanometer length scale. In our approach, we transport beams of energetic ions (1 to 200 keV) through small (5-30 nm diameters), high aspect ratio holes (>5:1) in the scanning probe tips. Holes are formed by Focused Ion Beam drilling and thin film deposition. Transport of single ions can be monitored through detection of secondary electrons that are emitted when ions impinge on sample surfaces. Secondary electron yield enhancements for highly charged dopant ions (e. g., P15+, or Te36+) allow efficient detection of single ion impacts for single atom device formation. Detection of secondary electrons and ions enables adaptation of a time-of-flight secondary ion mass spectrometry scheme for correlation of scanning probe images with chemical and molecular composition information on a 10 nm length scale. In our presentation we will discuss potential and limits of this approach in ion placement resolution, sensitivity in surface analysis, as well as issues of probe lifetime and effects of ion guiding in dielectric nanoholes. Acknowledgments: We thank the staff of the UC Berkeley Microlab, and the National Center for Electron Microscopy for their technical support. This work was supported by NSA and ARDA under ARO contract number MOD707501, and by the U. S. DOE under contract No. DE-AC03-76SF00098.

9:20am **NS1-ThM4 Fabrication and Electrical Characterization of 2D Dopant Nanoelectronic Devices in Si***, J.S. Kline, S.J. Robinson, J.R. Tucker,* University of Illinois at Urbana-Champaign*; J.-Y. Ji, T.-C. Shen,* Utah State University*; C. Yang, R.-R. Du,* University of Utah

The integration of nanoscale devices with Si-based microelectronics presents a major challenge in nanotechnology. We address this issue by employing STM patterned P donors as the building block for all-epitaxial nanoscale devices on pre-fabricated templates. To preserve the As-implanted contacts, we have developed a low-temperature UHV process using 300eV Ar ion sputtering and sub-700°C annealing to prepare atomically flat and clean surfaces for STM lithography. Differences in surface features and tunneling spectroscopy allow the registration of the STM to the template. After STM nanolithography, P donors are selectively deposited onto the patterned area by phosphine exposure. Subsequent Si low-temperature deposition and 500°C annealing forms an epitaxial overlayer and activates the dopant atoms. Electron transport measurements at 4.2K for several 2-terminal devices including two-dimensional P wires 10-50nm wide and 30-700nm long indicate resistivity of the wires is in the order of 20k@ohm@/sq. Quantum coherence length and the implication of the oscillations in the magnetoresistance at 0.3K will be discussed. In addition, the fabrication and measurement of tunnel junctions is currently in progress and will also be reported. This work is supported by DARPA-QuIST program under ARO contract DAAD 19-01-1-0324.

9:40am **NS1-ThM5 Scanning Tunneling Microscopy Electronic Characterization of a Nano Device for Quantum Computing***, M.E. Hawley, G.W. Brown, H. Grube,* Los Alamos National Laboratory

Quantum computation is a revolutionary new paradigm that has seen tremendous growth since 1994. The quest to build a quantum computer (QC) has been inspired by its recognized formidable computational potential. The long-term goal in this quest is a large scale, fast, parallel and easily fabricated QC. Although a number of ingenious schemes have been proposed, silicon-based solid-state proposals, using nuclear or electron spins of dopants such a phosphorus as qubits, are attractive because of the long spin relaxation times and their scaleability and integratability with existing silicon technology. We have been working on such a device based on a proposal by B. Kane (Nature 393, 133 (1998), in which buried P atoms placed 20 nm apart act as quantum bits entangled through exchange interactions, atomically placed using Scanning tunneling microscope (STM) lithographic techniques on a hydrogen resist layer. This effort requires dosing the Si(100) surface with phosphine molecules and annealing the phosphorus into the silicon surface. STM-based atomic level lithography methods provides us with the added capability of characterizing the local electronic environment of the dopants. In this talk, Iâ?Tll describe our particular effort to fabricate a QC and the charge imaging technique we are using to image buried phosphorus dopants and charged defects that could potentially interfere with the operation of such a QC device as well as any other nano scale device on the silicon surface.}

10:00am **NS1-ThM6 Nanotip Arrays Fabricated by One-step and Self-masked ECR-Plasma Etching and Their Applications for Field Emission, Antireflection and Sensing***, L.C. Chen, J.S. Hsu,* National Taiwan University, Taiwan*; H.C. Lo,* Academia Sinica, Taiwan*; I.F. Huang,* National Taipei University of Technology, Taiwan*; K.H. Chen,* Academia Sinica, Taiwan*; C.R. Lin,* National Taipei University of Technology, Taiwan*; C.F. Chen,* National Chiao-Tung University, Taiwan

Well-aligned nanotip arrays with a nanotip density as high as 10^12 cm^-2 were achieved by a single-step electron cyclotron resonance plasma process using gas mixtures of silane, methane, argon and hydrogen. Formation of SiC cap was observed on each individual nanotip, implying a self-mask etching mechanism. This dry-etching technique was applied to a variety of substrates such as Si, GaN, GaP, Al, sapphire and glass, indicating its general applicability. The nanotip arrays so produced showed superior field emission as well as antireflection properties. The extremely sharp tip geometry provides large field enhancement, therefore a low turn-on field (<1V/micron), while the sub-wavelength nanostrutured surface exhibits an ultra low reflectivity (<0.1%) in visible and IR. The latter property can be explained by a simple gradient index model. Furthermore, the nanotip arrays dispersed with Ag nanoparticles also showed excellent surface enhancement in Raman scattering (SERS). By optimizing the size of Ag nanoparticle and inter-particle distance, SERS of 8-order has been achieved, suggesting potential application of nanoparticle-dispersed nanotip arrays in molecular sensors.

10:20am **NS1-ThM7 Nanoscale Integration of NanoCarbons Based on Ultrananocrystalline Diamond and Carbon Nanotubes***, X.C. Xiao, O.H. Auciello, J.A. Carlisle,* Argonne National Laboratory

Nanostructured carbon materials exhibit excellent physical, chemical, mechanical, tribological, and electrical and thermal transport properties that are dictated by the many different bonding configurations available to carbon. Ultrananocrystalline diamond (UNCD) films, and carbon nanotubes (CNTs) are recently discovered nanocarbons with unique properties, and are of particular research interest and have many potential applications. Novel properties and applications could also be expected from the nanoscale integration of these two materials. We report in this study our approaches to strategically combine and control the carbon nanostructure consisting of UNCD and CNTs. Two approaches to the integration of UNCD and CNTs have been developed and the material properties evaluated. The first type is the self-assembly of carbon nanostructure based on UNCD and CNTs which were synthesized simultaneously using a single Ar/CH@sub4@ plasma chemistry in a microwave plasma chemical vapor deposition system. The ease to tailor the nanostructure through adjustment of the nucleation conditions (the relative fraction of nanodiamond seeds for growing UNCD and transition metal catalyst for growing CNTs) as well as the growth temperatures offers a new possibility to form carbon based self assembly nanostructures with unique combined mechanical and electronic properties. In the second approach CNTs are grown directly on UNCD thin films, again through the use of transition metal catalyst dispersed on the UNCD surface and the use of Ar/CH@sub4@ plasmas. The robust integration of vertically aligned CNTs on UNCD combined two desirable electrochemical properties of CNTs and UNCD, i.e. the high specific surface area from CNTs and electrochemical stability from UNCD. Preliminary structure characterization and property studies illustrated the potential of this structure to be used as electrochemical electrodes for chemical sensing applications and in supercapacitors.

10:40am **NS1-ThM8 The Role of Hydrogen in Ultrananocrystalline Diamond Thin Film Growth***, J.P. Birrell,* Argonne National Laboratory, U.S.*; J.E. Gerbi, O.H. Auciello, J.A. Carlisle,* Argonne National Laboratory

A great deal of recent experimental studies and computer simulations have been performed to try to understand the surface stability of diamond nanocrystals. These results have yielded a number of striking conclusions that and the size of the crystallite. This study can help explain the transition of diamond thin film structure from microcrystalline to nanocrystalline with the reduction of hydrogen in the gas phase during microwave plasma enhanced chemical vapor deposition; namely, that the stability of the surface of the diamond nanoparticle is a strong function of both the hydrogen coverage uses TEM, Raman scattering, and XRD to investigate the role of hydrogen in the growth of ultrananocrystalline diamond (UNCD) thin films in two different regimes. First, we add hydrogen to the normal Ar/CH@sub 4@ gas mixture used during growth, and observe that rather than a monotonic increase in the grain size from nanocrystalline to microcrystalline, the films are clearly mixed-phase, with microcrystalline diamond inclusions that become much more prominent with added hydrogen. Second, we remove hydrogen from the plasma by changing the hydrocarbon precursor from CH@sub 4@ to C@sub 2@H@sub 2@. We observe that there is a lower limit to the amount of hydrogen that needed to sustain ultrananocrystalline diamond growth, below which a significant amount of disordered graphitic carbon is nucleated. We suggest that the reasons for these observed changes are that large amounts of hydrogen (in the form of H@super +@) in the plasma enables the more rapid growth of diamond microcrystals, while low concentrations of hydrogen result in unstable diamond nanocrystals and thus the nucleation of disordered carbon material. This work was supported by the DOE-Office of science-Materials Science under Contract No. W-31-109-ENG-38.

11:00am **NS1-ThM9 Surface-Templated Assembly of Nanoparticles on Solid Surfaces for Nano-Optical Applications***, **S. Myung**, N. Cho, J. Kim, D. Kim, S. Hong,* Seoul National University, South Korea

Nanoparticles made of CdSe or Au have been extensively utilized for optical labeling and other nano-optical applications. In this case, one technological challenge can be positioning nanoparticles onto desired locations on solid substrates with a nanometer scale precision. We utilized surface-templated assembly strategy to position Au and CdSe nanoparticles onto specific locations on Au and silicon oxide substrates. In our method, thiol-terminated self-assembled monolayer (e.g. MPTMS) patterns are utilized to capture nanoparticles from the solution, while methyl-terminated SAM (e.g. 1-octadecanethiol) patterns are utilized to avoid any unwanted assembly of nanoparticles. We also explored the possibility of assembling fluorescent nanoparticles onto 3D structures such as AFM tip for nano-optical applications.

Nanometer-scale Science and Technology
Room 213D - Session NS2-ThM

Nanowires I

Moderator: T.S. Mayer, Penn State University

8:20am **NS2-ThM1 MOCVD Synthesis of Group III Nitride Nanowires and Heterostructure Nanowires***, **G.T. Wang**, J.R. Creighton, P.P. Provencio, W. Pan,* Sandia National Laboratories

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. To date, the primary growth methods used to synthesize GaN nanowires have been thermal evaporation or chemical vapor deposition techniques using Ga metal or GaN powder source materials in hot-wall tube reactors. These evaporation-based techniques suffer from a general lack of control, reproducibility, scalability, and the ability to produce complex heterostructures. Metal-organic chemical vapor deposition (MOCVD) has achieved widespread commercial adoption for the growth of III-nitride films and devices, with the demonstrated ability to produce complex heterostructures and doping. We have employed a MOCVD process to synthesize GaN nanowires in a standard cold-wall rotating disk reactor on 2-inch diameter wafer substrates coated with Ni catalysts. TEM, EDS, and photoluminescence studies indicate that the nanowires are single-crystalline GaN with Ni clusters at the tips, indicating growth via the vapor-liquid-solid (VLS) mechanism. The nanowires have tip diameters typically from 20-100 nm and lengths of up to tens of microns. We have also been able to synthesize core-shell heterostructure nanowires consisting of a GaN cores and various III-nitride shell materials, including AlN, InN, and AlGaN, and InGaN. 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. The optical and electrical properties of single nanowires and heterostructure nanowires along with the challenges of the MOCVD nanowire growth process will also be discussed.

8:40am **NS2-ThM2 Ultralong and Portable Semiconductor Nanowire Arrays***, **Q. Li**, E.C. Walter, W. van der Veer, R.M. Penner,* University of California, Irvine

Long semiconductor nanowires, organized into parallel arrays, are desirable for a variety of nanoelectronic applications. Most of the current synthesis methods produce nanowires that are randomly distributed and effort must be expended to organize the nanowires onto solid surface for electronic applications. Here we propose a hybrid electrochemical/chemical method for the synthesis of millimeter-long semiconductor nanowires that are organized into arrays on solid surface. Our method involves two steps: First, electrochemical step edge decoration was adopted to obtain the precursor nanowires on highly oriented pyrolytic graphite (HOPG). Second, the as-deposited nanowires were chemically converted to semiconductor nanowires. MoS@sub 2@ nanowire arrays, a semiconductor material stable in moist air up to 80@super o@C, were synthesized by heating electrodeposited MoO@sub 2@ nanowires in H@sub 2@S at elevated temperatures. The nanowires were characterized by TEM, SEM and XRD. Two discrete structures were observed depending on the conversion temperature. For nanowires annealed at or below 700@super o@C, the MoS@sub 2@ nanowires were composed of randomly distributed 5-10 atomic layer thick MoS@sub 2@ ribbons. For nanowires annealed at 800@super o@C, MoS@sub 2@ atomic layers oriented parallel to the HOPG basal plane. Their diameters were easily controlled by their precursor MoO@sub 2@ nanowires. The electronic and optical properties were probed by transferring the nanowires onto suitable surfaces. Conductivity in both types of wires was thermally activated and the thermal activation energy was tuned from 125meV (700@super o@C annealing) to 25meV (800@super o@C annealing), lower than the reported MoS@sub 2@ thin films. The optical adsorption spectra showed two excitons, which blueshifted as a function of nanowire thickness due to the quantum confinement. Such organized and portable nanowire arrays are promising for nanoelectronics applications.

9:00am **NS2-ThM3 Fabrication of Gold Nanowires by Non-contact Atomic Force Microscopy***, **M.E. Pumarol**, Y. Miyahara, P. Grutter,* McGill University, Canada

Interfacing nanostructures to the macroscopic world is fundamental for their study and possible electronic applications. SPM-based metal deposition techniques are an attractive approach for this goal: due to their easy implementation and the possibility of a maskless direct modification of the surface. These techniques exploit the very intense electric field that appears when an SPM tip is in close proximity with a surface and a potential difference is applied. Here we use a commercial AFM operated in a dynamic mode and in ambient conditions for direct writing /patterning of gold nanowires. For their fabrication, voltage pulses of 20 â?" 30V are applied to a gold coated AFM tip and an insulating surface with a finite tip-surface gap of several nanometers. This produces gold dots with lateral dimensions from under 10 nm to 100 nm, and by increasing the deposition duty cycle dots are overlapped to form a nanowire. Control of the tip sample separation is critical to ensure the reliability and reproducibility of the deposition process. In this work, we use an innovative non-contact based technique to precisely control this separation and by extension the electric field. An advantage of this method of deposition is the ability of locating the part of the sample to which the nanowire will be contacted / attached. Here, we bridge gold macro-electrodes, deposited by EBL, by forming a nanowire between them. A new way for overcoming proximity effects of the AFM tip with a protruding electrode is presented. In the future, this technique will be useful for attaching contact leads to nanostructures like q-dots, nanodots, nanoparticles, and others.

9:20am **NS2-ThM4 Controlled Polymerization of Substituted Diacetylene Self-assembled Monolayers Confined in Molecule Corrals***, T.P. Beebe, Jr.,* University of Delaware*; A. Schnieders,* ION-TOF USA, Inc.*; **S.P. Sullivan**,* University of Delaware

The ever growing need to further miniaturize integrated circuits has lead to an increase in research on nanoelectronics. We have shown that it is possible to directly polymerize self-assembled 10, 12-tricosadiynoic acid (TCDA) adsorbed on highly oriented pyrolytic graphite (HOPG) at the solid/liquid interface using a Scanning Tunneling Microscope (STM) tip. Polymerized oligomers are formed at a predefined point where a voltage pulse is applied while operating in Scanning Tunneling Spectroscopy (STS) mode. The oligomers can be confined and controlled on the nanometer scale using molecule corrals created on the substrate via ToF-SIMS Cs@super +@ ion bombardment. In over ~ 150 observations polymerized oligomers never extended over domain boundaries or corral edges, providing natural connection points to possibly test the electrical properties of the nanowires. The quasi-infinite supply of diacetylene molecules remaining in the covering solution enables a dynamic exchange of molecules to the surface. This exchange occurred on approximately the same time scale (10@super -1@ s) as it does to collect one image, and depends weakly on the length of the desorbing oligomer. The desorption is thus likely influenced by tip-surface interactions as is often the case in STM experiments. A theoretical model is currently being developed to further our understanding of the effect of oliogmer length on the rate of oligomer desorption from the HOPG surface.

9:40am **NS2-ThM5 Semiconducting Nanowires - Synthesis, Characterization and Novel Properties*, S.-T. Lee,*** City University of Hong Kong, China **INVITED**

Oxide-assisted growth (OAG) via thermal evaporation is introduced to produce large-quantity, high-purity (no metal contamination) silicon nanowires. OAG is a generic synthetic method that can produce a host of one-dimensional semiconducting nanowires, including those of Group VI (Ge, C, SiC), III-V (GaN, GaAs, GaP) and II-VI (ZnO, ZnS, ZnSe) elements. Silicon nanowires are produced with controlled diameter, desired orientation or pattern, and morphology (wire, chain, ribbon, cable). The structural, optical, electronic, and chemical properties of silicon nanowires have been characterized. Atomically-resolved STM images revealed detailed atomic structure of Si nanowires, while STS measurements demonstrated quantum size effect in the bandgap of Si nanowires. Regular arrays of intramolecular junctions in Si nanowires are shown to exhibit sharp conductivity changes across junctions. Si nanowires give strong polarized green-red emission, and exhibit interesting chemical and sensing properties. We further show properly assembled nanowires possess strong photoluminescence and lasing properties. The results offer exciting opportunities for research and applications in nanoscience and nanotechnology.

10:20am **NS2-ThM7 Strain Mapping in Nanowire Heterostructures*, J.L. Taraci,*** Arizona State University*; M.J. Hÿtch,* Centre National de Recherche Scientifique, France*; T. Clement, J.W. Dailey, D.J. Smith, P. Peralta, J. Drucker, S.T. Picraux,* Arizona State University

A new method for the detailed strain analysis of nanowires and nanowire heterostructures will be discussed. This technique enables strain mapping of nanowires based on the combination of high resolution electron microscopy and image analysis. The accuracy to which strain may be determined using this method is better than 0.3%, which allows for the accurate strain mapping of core-shell and heterostructure nanowires. The technique is applied to nanowires grown by vapor-liquid-solid CVD using disilane and digermane. We will show how this technique can be used to obtain detailed distributions of @epsilon@@sub xx@, @epsilon@@sub yy@, @epsilon@@sub xy@, mean dilatation, and rotation maps within individual nanowire heterostructures. We first demonstrate the method by analysis of a single Ge nanowire which displayed a linear rotation along the growth axis, with the nanowire in compression and tension on either side of the central axis. The measured results are shown to be in agreement with a nanomechanics description of the nanowire for a bending moment applied at the end of the cantilevered nanowire beam. We then present preliminary results for Si-Ge core-shell and heterointerface nanowires. This technique allows for the direct strain mapping at heterostructure interfaces due to the lattice mismatch. In these studies the Si/Ge growth is carried out at 400°C and below to minimize any chemical interdiffusion effects on the strain profiles. The resulting strain maps of nanowire heterostructures can then be directly compared with Stillinger Weber modeling of the anticipated Si-Ge strain distributions, assuming chemically abrupt interfaces. The large aspect ratio nanowire structures allow rapid lateral relaxation with distance from the interface and thus provide an interesting contrast to conventional strained layer heterostructures.

10:40am **NS2-ThM8 Direct Atomically Resolved Imaging inside a Nanowire*, A. Mikkelsen,*** *N. Skold, L. Ouattara, M. Borgstrom, J.N. Andersen, L. Samuelson, W. Seifert, E. Lundgren,* Lund University, Sweden

Semiconductor nanowires are perceived as future components in nanoelectronics and photonics. Applications, such, bio/chemical sensors , n- p- type diode logic and single nanowire lasers have already been realized in the laboratory. Because of the extremely small dimensions of a nanowire, atomic scale structural features can have a significant impact on their properties. The large surface to bulk ratio of tailor-made nano-crystallites and low dimensional systems as compared to usual bulk crystals can result in new crystal structure and morphology not found in bulk equivalents. Therefore, structural methods that address these issues are highly desirable. One such method is Scanning Tunneling Microscopy (STM) that has revolutionized our perception nano-scale objects and low-dimensional systems. In this study we demonstrate a new powerful method to image individual atoms inside freestanding III-V semiconductor nanowires using a combination of Cross-Sectional Scanning Tunneling Microscopy and a novel embedding scheme. We image areas of the nanowire with atomic resolution both along the wire, and through the face of the wire. Utilizing this method we for example image the individual atoms in planar twin segments of the wire and show that individual atomic impurities in a GaAs nanowire can be imaged. Finally we image the GaAs nanowire at the substrate interface revealing intriguing details about the initial growth of the nanowire.

11:00am **NS2-ThM9 Time-Resolved X-Ray Excited Optical Luminescence Studies of Semiconductor Nanowires@footnote 1@*, R.A. Rosenberg,*** *G.K. Shenoy,* Argonne National Laboratory*; S.T. Lee,* University of Hong Kong, China*; F. Heigl,* Canadian Synchrotron Radiation Facility*; P.-S.G. Kim, X.-T. Zhou, T.K. Sham,* University of Western Ontario, Canada

Due to quantum confinement effects nanostructures often exhibit unique and intriguing fluorescence behavior. X-ray excited optical luminescence (XEOL) provides the capability to chemically map the sites responsible for producing low energy (1-6 eV) fluorescence. By taking advantage of the time structure of the x-ray pulses at the Advanced Photon Source (APS, ~80 ps wide, 153 ns separation) it also possible to determine the dynamic behavior of the states involved in the luminescence. In this presentation we show how this technique can be utilized to understand the XEOL from silicon nanowires (~14 nm diameter) and show preliminary results from studies of II-VI nanoribbons. Previous XEOL studies of silicon nanowires have revealed luminescence in the 400-700 nm region.@footnote 2@@super ,@@footnote 3@ The lower wavelength part of the spectrum is associated with the oxide shell while longer wavelength emission is due to the silicon core. The present results support these findings. In addition we find that the longer wavelength, silicon core emission has a relatively short lifetime (<10 ns) while the oxide shell fluorescence has a much longer lifetime. These results will be discussed in terms of prior time-resolved work on porous silicon and related systems. In addition we plan to present initial results from studies of ZnS, ZnTe, CdSe and CdS nanoribbons. @FootnoteText@ @footnote 1@Work supported by U.S. Department of Energy, Office of Basic Energy Sciences under Contract No. W-31-109-ENG-38.@footnote 2@X.-H. Sun, Y.-H. Tang, R. Zhang, S.J. Naftel, R. Sammynaiken, T.K. Sham, H. Y. Peng, Y.-F. Zhang, N.B. Wong, and S.T. Lee, J. Appl. Phys. 90, 6379 (2001).@footnote 3@T.K. Sham, S.J. Naftel, P.-S. G. Kim, R. Sammynaiken, Y.H. Tang, I. Coulthard, A. Moewes, J.W. Freeland, Y.-F. Hu, S.T. Lee, Phys. Rev. B, to be published.

11:20am **NS2-ThM10 Mechanical and Electromechanical Behaviour of Li@super +@(Mo@sub 3@Se@sub 3@)@super -@ Nanowires and Nanowire Bundles*, A. Heidelberg,*** Trinity College Dublin, Ireland*; J.W. Schultze,* Heinrich-Heine-Universität Düsseldorf, Germany*; J.G. Sheridan, B. Wu, J.J. Boland,* Trinity College Dublin, Ireland

Li@super +@(Mo@sub 3@Se@sub 3@)@super -@ forms quasi-1D crystals and is structurally related to the Chevrel phases @footnote 1@. It can be viewed as a condensation polymer of (Mo@sub 3@Se@sub 3@)@super -@ units. In the crystal the {(Mo@sub 3@Se@sub 3@)@super -@}@sub n@ strands are separated by Li@super +@ counterions. The crystals dissolve in polar solvents with @epsilon@ > 45 yielding conductive polyelectrolytes. From solution conductive single nanowires with a diameter of 0.6 nm and bundles of nanowires were deposited on substrate surfaces. The bundle height is typically between 10 and 100 nm and the length exceeds 5 @micron@ @footnote 2@. Mechanical measurements on Li@super +@(Mo@sub 3@Se@sub 3@)@super -@ nanowire bundles with a height range between 25 and 200 nm have been carried out using a SPM-nanomanipulator. For the experiments nanowires were deposited out of solution across trenches on SiO@sub 2@. The trench depth was typically between 100 and 300 nm and the width between 1 and 3 @micron@. To prevent any slippage of the nanowires 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. The size of the Pt lines varied depending on the size of the wire of interest. Lateral manipulations on nanowire bundles yielded force traces. Taking into account the wire shape and dimensions as well as the AFM cantilever dimensions, the Youngs modulus, the yield strength and the maximum bending strength of the nanowires can be obtained from the force traces. The Youngs modulus for Li@super +@(Mo@sub 3@Se@sub 3@)@super -@ nanowires has been measured to be in the range of 500 to 600 GPa. The electromechanical properties of nanowire bundles under mechanical stress were also measured. @FootnoteText@ @footnote 1@ R. Chevrel, M. Sergent, J. Prigent, J. Solid

State Chem 3 (1971) 515 @footnote 2@ A.Heidelberg, J. W. Schultze, C. J. Booth, E. T. Samulski, J. J. Boland, Z. Phys. Chem. 217 (2003) 573.

11:40am **NS2-ThM11 Strong Field Emission of Taper-Like and Rod-like Si Nanowires Grown on Si@sub X@Ge@sub 1-X@ Substrate***, **Y.-L. Chueh,*** National Tsing Hua University, Taiwan*; L.J. Chou,* National Tsing Hua University, Taiwan, Republic of China*; S.L. Cheng, J.H. He, W.W. Wu,* National Tsing Hua University, Taiwan*; L.J. Chen,* National Tsing Hua University, Taiwan, Republic of China

Taper-like and rod-like Si nanowires (SiNWs) have been synthesized on Si and Si@sub 0.8@Ge@sub 0.2@ substrate annealed at 1200 °C in N@sub 2@ ambient. The tip regions of taper-like SiNWs are about 5-10 nm in diameter. The average length of the taper-like SiNWs is about 6 µm with aspect ratios is around 150-170. On the other hand, the rod-like is 5-100 nm in diameter, and 4-5 µm in length. The proposed growth models of there nanowires are oxide-assisted growth (OAG) and vapor-liquid-solid (VLS) growth. The taper-like morphology may be created by the passivation of the SiO@sub 2@ coating layer, and resulted in the different levels of absorption of SiO along the nanowires. The formation of metal-catalyst free rod-like SiNW is due to creation of unstable thin SiO@sub x@ layer, which vaporized easily during the annealing process. The optical and field emission characterization of these SiNWs have been investigated and present. Taper-like Si nanowires exhibit a superior field emission with a turn-on field of 6.3-7.3 V/µm and a threshold field of 9-10 V/µm. The @beta@ value are estimated to be 700 and 1000 at low and high fields, respectively. The excellent field emission characteristics are attributed to the perfect crystalline structure and taper-like geometry of the Si nanowires.

Organic Films and Devices
Room 304C - Session OF+NS-ThM

Molecular Electronics

Moderator: X.-Y. Zhu, University of Minnesota

8:20am **OF+NS-ThM1 Molecular Engineering to Test the Mechanism of Conductance Switching for a Variety of Conjugated Molecules***, **A.M. Moore**, B.A. Mantooth, A.A. Dameron, Z.J. Donhauser,* The Pennsylvania State University*; J.W. Ciszek, F. Maya, Y. Yao, J.M. Tour,* Rice University*; P.S. Weiss,* The Pennsylvania State University

Phenylene ethynylene oligomers have been studied as candidates for molecular electronic devices using scanning tunneling microscopy.@footnote 1-6@ These molecules were inserted into host alkanethiolate self-assembled monolayers for isolation and individual addressability. Many different hypotheses and theoretical predictions have been put forth to describe conductance switching.3-4 We have tested several of these through variations in the molecular design of our molecular switches and have concluded that the only mechanism consistent with all the switching data are that changes in the molecule-substrate bond hybridization leads to the observed conductance changes. @FootnoteText@ @footnote 1@Donhauser, Z. J.; Mantooth, B. A.; Kelly, K. F.; Bumm, L. A.; Monnell, J. D.; Stapleton, J. J.; Price, D. W.; Rawlett, A. M.; Allara, D. L.; Tour, J. M.; Weiss, P. S. 2001, Science 292, 2303.@footnote 2@Donhauser, Z. J.; Mantooth, B. A.; Pearl, T. P.; Kelly, K. F.; Nanayakkara, S. U.; Weiss, P. S. 2002, Jpn. J. Appl. Phys. 41, 4871.@footnote 3@Mantooth, B. A.; Weiss, P. S. 2003, Proc. IEEE 91, 1785.@footnote 4@Moore, A. M.; Dameron, A. A.; Mantooth, B. A.; Yao, Y.; Ciszek, J. W.; Maya, F.; Tour, J. M.; Weiss, P. S. 2004, Nanotechnology In press.@footnote 5@Lewis, P. A.; Inman, C. E.; Yao, Y. X.; Hutchison, J. E.; Tour, J. M.; Weiss, P. S. In Preparation.@footnote 6@Dameron, A. A.; Ciszek, J. W.; Tour, J. M.; Weiss, P. S. In Preparation.

8:40am **OF+NS-ThM2 Room Temperature Molecular Memory Observed from a Nanowell Device***, N. Gergel,* ***N. Majumdar,*** University of Virginia*; K. Keyvanfar, N. Swami,* University of Virgina*; L.R. Harriott, J.C. Bean,* University of Virginia

Researchers are debating whether the electrical switching behavior observed from some molecular devices can be attributed exclusively to the molecules@footnote 1@. We tested an OPE molecule with a nitro side group. This molecule showed electrical switching behavior when tested in a nanowell device at room temperature. This behavior was not seen when testing a simple conjugated molecule that lacked the nitro group. The test was performed in a nanowell device that consisted of a monolayer of molecules self-assembled on an area of gold 10-40 nm in diameter and capped with titanium and gold@footnote 2@. The I-V characteristics of the nitro molecule clearly showed two distinct conductivity states with a current ratio of 5 to 1 at room temperature. The experimental data showed that at a particular threshold voltage, the output current changed from a high current state to a low current state. This change in state was reversed with the opposite applied voltage. Hysteresis was not observed when testing a similar conjugated molecule without the nitro group at room temperature. Thus, the switching behavior could be attributed to changes in the conductivity of the nitro molecules due to the applied voltage. Other groups have reported seeing negative differential resistance behavior (NDR) in the I-V characteristics of the nitro molecule@footnote 3@. We saw similar peaks to those reported. However, our investigations indicate that this behavior is not reversible without the application of a negative threshold voltage. For this reason, these molecules may not be suitable for classic NDR circuits (e.g. Goto pairs@footnote 4@). This hysteretic behavior may nevertheless have device potential. @FootnoteText@ @footnote 1@ R.F. Forrest, Science 302, 556 (2003).@footnote 2@N. Majumdar, et al, submitted to J. Vac. Sci. Tech.@footnote 3@ M.A. Reed, et al, Applied Physics Letters 78, 3735 (2001).@footnote 4@ G. Rose, and M. Stan, IEEE NANO, San Fransisco, Aug (2003).

9:00am **OF+NS-ThM3 Metal/Molecule/Metal and Metal/Molecule/Semiconductor Device Structures***, **D. Janes,*** Purdue University **INVITED**

This talk will describe the development and electrical characterization of two classes of molecular electronic components. The first class of structures involves metal-molecule-metal systems with pre-formed metal contacts, primarily lateral break junctions formed either by electromigration or by shadow evaporation. A number of molecular species have been studied using these structures, including short aromatic thiols and short DNA double strands with thiol bonding groups at each end. The electrical characteristics of these devices indicate that strong coupling between the contacts and the molecular species can be realized. The second class of devices involves metal/molecule/semiconductor device structures, which are lithographically defined and fabricated using an indirect evaporation technique for the metal (top) contact and p+ GaAs for the bottom contact. In these structures, the electronic conduction between the metal and semiconductor can be modulated by choice of molecular species. Several alkyl thiol and aromatic thiol molecules have been employed in order to determine the effects of molecular length, conjugation and intrinsic dipole moment. The current-voltage characteristics and conductance versus temperature both indicate that the molecular layers change the transport mechanism, generally involving a lower effective barrier height than that of a metal/semiconductor Schottky barrier. These results reflect previous studies in which nanoscale metal/molecule/semiconductor structures exhibited low resistance contacts, implying that effective coupling and control of the surface electrical properties can be achieved using a molecular layer.@footnote 1@ A simple model for the conduction has been developed, utilizing our prior studies on surface Fermi level unpinning in GaAs structures.@footnote 2@ @FootnoteText@ @footnote 1@ T. Lee, et al., APL 76, 212 (2000). @footnote 2@ S. Lodha, et al., Appl. Phys. Lett. 80, 4452 (2002).

9:40am **OF+NS-ThM5 Room Temperature Negative Differential Resistance Measured through Molecular Monolayers Adsorbed to Silicon Surfaces with Ultra-high Vacuum Scanning Tunneling Microscopy***, **N.P. Guisinger**, R. Basu, M.E. Greene, A.S. Baluch, M.C. Hersam,* Northwestern University

In recent years, substantial progress has been made in the emerging field of molecular electronics. In particular, metal-molecule-metal junctions have been widely studied. In this paper, a continued study of charge transport through molecule-semiconductor junctions is considered. The presence of the energy band gap in semiconductors provides opportunities for resonant tunneling through individual molecules, leading to interesting effects such as room temperature negative differential resistance (NDR).@footnote 1@ In this study, the ultra-high vacuum scanning tunneling microscope was used to probe charge transport through two different molecular monolayers adsorbed to the Si(100) substrate. I-V measurements were taken on monolayers of TEMPO and cyclopentene for both degenerately doped n-type and p-type Si(100) substrates. Initial I-V measurements through the TEMPO monolayer exhibited a suppression of NDR behavior relative to previously reported transport through isolated molecules.@footnote 1@ I-V measurements were also taken on isolated cyclopentene molecules, as well as on cyclopentene monolayers. The cyclopentene monolayers similarly exhibited a suppression of the observed NDR behavior relative to transport through isolated molecules. For both molecular monolayers, the suppression of the peak-to-valley ratio (PVR) has been measured to exceed a 47 percent reduction compared to observed PVRs of isolated molecules. The resulting NDR suppression in both monolayers indicate that the local environment surrounding the molecules strongly influences charge transport. In addition to molecular monolayers, initial studies of transport through isolated TEMPO molecules adsorbed to both degenerate and non-degenerate Si(111) will be discussed. @FootnoteText@ @footnote 1@N. P. Guisinger, M. E. Greene, R. Basu, A. S. Baluch, and M. C. Hersam, "Room temperature negative differential resistance through individual molecules on silicon surfaces," Nano Letters, 4, 55 (2004).

10:00am **OF+NS-ThM6 Two Distinct Types of Switching Behavior in a Single Molecule**, ***A.S. Blum***, *J.G. Kushmerick, C.H. Patterson,* Naval Research Laboratory; *J.C. Yang,* Duke University; *J.C. Henderson, Y. Yao, J.M. Tour,* Rice University; *R. Shashidhar,* Geo-Centers, Inc.; *B.R. Ratna,* Naval Research Laboratory

There is recent controversy surrounding the ability of molecules to function as switches in molecular electronic devices. We report the observation of two distinct types of switching in matrix isolated and complete monolayers of bipyridyl-dinitro-oligophenylene-ethynylene (BPDN). Extensive measurements in a scanning tunneling microscope (STM) demonstrate both stochastic and voltage driven switching in this molecule, representing the first description of two distinct types of switching in a single molecule. While stochastic switching has been reported for several molecular systems, we argue that the observed voltage controlled switching is a distinct physical event specific to BPDN. Furthermore, consistent switching behavior measured with both a scanning tunneling microscope and a crossed-wire tunnel junction demonstrates that the switching is intrinsic to the molecule and is not an artifact of the measurement system.

10:20am **OF+NS-ThM7 Electrical and Mechanical Contacts at the Atomic Scale: a Combined UHV STM/AFM Study**, ***Y. Sun***, *M. Henrik, S. Schaer, Y. Miyahara, A.-S. Lucier, M.E. Ouali, P. Grutter,* McGill University, Canada; *W. Hofer,* University of Liverpool, United Kingdom

Understanding electrical contacts is widely considered as one of the central issues in molecular electronics. As a first step, we have measured simultaneously at the atomic scale the interaction forces and the currents between a sharp tungsten tip and a Au(111) sample using a combined ultra-high vacuum scanning tunnelling and atomic force microscope (UHV STM/AFM). Close correlation between conductance and interaction forces were observed in the regimes from weak coupling to strong interaction. In particular, the electrical and mechanical points of contact are defined as a result of the observed barrier collapse and adhesive bond formation, respectively. The points of contact as defined by force and current measurements coincide within measurement error. We find experimentally that at contact the very front atoms of the tip apex experience repulsive forces, while the total interaction force remains attractive as a consequence of competing interaction decay lengths. Ab-initio calculations of the current as a function of distance were performed for our experimental tip-sample system. We find that in the weak coupling regime the calculated electrical current as a function of distance is in quantitative agreement with experimental results only if tip and sample relaxation effects are taken into account. The calculated relaxation of the tip apex atoms is 50-100 pm. We conclude that force effects of different decay lengths cannot be excluded if a detailed understanding of atomic scale contacts is to be achieved.

10:40am **OF+NS-ThM8 Structure of Self-Assembled Monolayers on Platinum**, ***D.Y. Petrovykh***, University of Maryland, Naval Research Laboratory; *H. Kimura-Suda, A. Opdahl, L.J. Richter, R.D. Van Zee, M.J. Tarlov,* National Institute of Standards and Technology; *L.J. Whitman,* Naval Research Laboratory

We studied formation of self-assembled monolayers (SAMs) on polycrystalline platinum thin films using X-ray photoelectron spectroscopy (XPS), Fourier transform infrared spectroscopy (FTIR), spectroscopic ellipsometry, and contact angle measurements. In particular we are interested in properties of SAMs on Pt with respect to their possible use as a substrate for Si-compatible molecular electronics. We find that SAMs formed on piranha-cleaned Pt from ethanoic solutions of n-alkanethiols have initial quality comparable to or better than that achieved under other conditions. The FTIR and XPS data indicate that films are formed with nearly normal orientation of alkane chains, have higher packing density than comparable SAMs/Au, and remain stable in ambient air for 3-5 days. XPS spectra of the S 2p region also show that SAMs/Pt are distinctly multicomponent. The main component, with the lowest binding energy, unambiguously corresponds to alkanethiol molecules adsorbed on Pt in a configuration similar to that for SAMs/Au. The minority higher binding energy components are not affected by exposure to good solvents and thus appear to correspond to different binding configurations related to surface roughness and oxidation (rather than to physisorbed molecules). Our results suggest that the use of oxide-free and atomically smooth Pt substrates may be necessary to attain a single-component, high-quality SAM on Pt.

11:00am **OF+NS-ThM9 Oligomer Length Dependent Study of Metal-Molecule Interactions in Model Molecular Wire Systems**, ***C.D. Zangmeister***, NIST, US; *S.W. Robey, R.D. Van Zee,* NIST

Interactions at the molecule-contact interface perturb the molecular orbitals important for electron transport in conjugated systems. These perturbations are particularly important for the nanometer size junctions applicable in molecular-scale electronics. This study looks at the variation of the occupied electronic structure of fully conjugated model molecular wire compounds as a function of molecular length. Specifically, the number of phenyl rings was varied from a single ring to three rings in unsubstituted phenylene ethynylene monolayers chemisorbed on Au using ultraviolet photoemission spectroscopy. This provides a qualitative picture of the extent of perturbation of the electronic structure due to thiol coupling and the variation of the molecular @pi@ levels important for electron transport as a function of the degree of conjugation. These data show a shift towards the Au Fermi levels in the @pi@ levels by more than an eV as the conjugation length is increased. These observations will be discussed in terms of previous electron transport investigations of these compounds adsorbed on Au.

11:40am **OF+NS-ThM11 Electrical Properties of DNA Characterized by Conducting-Atomic Force Microscopy**, *C. Nogues,* ***S.R. Cohen***, *S. Daube, R. Naaman,* Weizmann Institute of Science, Israel

DNA has been widely promoted as the key component of future molecular devices, due to its unique assembly and recognition properties. Specifically, the strong interaction between complementary base-pair sequences on interacting DNA strands can be utilized to self-assemble a desired structure in a molecular circuit. The most basic building blocks of such circuits can be formed through the hybridization of two single strands into a double one, and the specific binding of functionalized DNA strands to gold electrodes using the chemical thiol-gold linkage. Such manipulations can exploit the ease in which DNA strands can be synthesized, and modified chemically. Despite these advantages, the electrical properties of individual strands of DNA have yet to be reproducibly characterized, due to the inherent difficulties in reliably accessing and measuring single molecules. We have attacked this problem by developing protocols for reproducible formation and characterization of DNA monolayers, and then probing their electrical functioning using conducting atomic force microscopy (cAFM). The electrical contact to the DNA was made by chemical binding to a gold electrode on one end, and to a gold nanoparticle on the other. Thus, repeatable measurements of the conductivity of individual DNA strands have been performed. Meaningful differences could be detected between conductivity in single- and double-strand DNA. The single strand DNA was found to be insulating over the range of -2 to +2 V, while the double strand DNA passes significant current outside a 3 eV gap.

Plasma Science and Technology
Room 213A - Session PS-ThM

Atmospheric and Microdischarges

Moderator: L. Bardos, Uppsala University, Sweden

8:20am **PS-ThM1 Atmospheric and Micro Discharges**, ***J.K. Lee***, Pohang University of Science and Technology, South Korea, S. Korea; *S.S. Yang, M. Radmilovic-Radjenovic,* Pohang University of Science and Technology, South Korea; *S. Mukherjee,* Pohang University of Science and Technology, South Korea, S. Korea **INVITED**

Plasma display panels (PDPs) are micro discharges, operated at high pressures of 400-500 Torr. Using 2-D kinetic simulation code (XOOPIC), we calculated incident angle and energy distributions of ions on the cathode surface in a PDP cell. Kinetic results show that in a coplanar-type PDP cell, most ions impinge on the MgO surface at the cathode region with the incident angle in the range of 10~30 degrees@footnote 1@ from normal with energies below 50 eV and two temperatures 5 and 50 eV. The calculated electron temperature at the anode striation@footnote 2@ region is lower than that between the striation bunches and ranges from 0.5 to 2 eV. We operated the panel at pressures in atmospheric range to study the distinction in the characteristics of the discharge. At a constant pd value by increasing pressure p (in the atmospheric pressure range) and reducing gap length d, we observed similar discharge characteristics to the conventional PDP. We also investigated the difference in the discharge characteristics in the presence and absence of radiation trapping@footnote 3@ and dimers by our 2-D and 3-D fluid simulations and the Paschen breakdown characteristics of microdischarges at high pressures. @FootnoteText@ @footnote 1@ S.S. Yang, J.K. Lee, et al., Contri. to Plasma Phys. (to appear in 2004).@footnote 2@ C.H. Shon and J.K. Lee, Phys. Plasmas 8, 1070 (2001).@footnote 3@ H.C. Kim, S.S. Yang, and J.K. Lee, J. Appl. Phys. 93(12), 9516 (2003).

9:00am **PS-ThM3 Gas and Electrode Temperatures in Non-equilibrium Atmospheric Pressure Plasma with Microwave Excitation***, **M.N. Nagai,*** Nagoya University, Japan

Gas and Electrode Temperatures in Non-equilibrium Atmospheric Pressure Plasma with Microwave Excitation Plasma processing is the most attractive industrial technology because etching, deposition, or synthesis processings of materials are able to be performed at the low temperature. Recently, atmospheric pressure non-equilibrium plasmas expand the application in not only conventional but also new industrial and science fields. To produce non-equilibrium plasmas, several attempts have been proposed, such as corona discharges and dielectric barrier discharges. The neutral gas temperature is one of the most important plasma parameters for producing non-equilibrium atmospheric pressure plasma. The gas temperature measured gives us the information concerning the chemical reaction in the plasma such as combination and elimination reaction. Excess high gas temperature causes the evaporation of electrodes for producing the plasma, and the melting of materials by the plasma irradiation. In this study, non-equilibrium atmospheric pressure plasma was successfully produced in N@sub 2@, Ar, or He gas using a dielectric barrier micro-gap plasma with microwave excitation. We investigated effects of pulse discharge and electrode temperature on gas temperature. We measured gas temperature by N@sub 2@ optical emission of the second positive band system and electrode temperature by blackbody emission. It was found that the short pulse modulation of microwave power and water-cooled electrode were effective for reducing the gas temperature. The pulse discharge decreased the gas temperature from 900 K to 600 K, and the water-cooled electrode decreased the gas temperature by more than 200 K. Controlling of the electrode temperature was one of the most effective techniques to reduce the gas temperature because the gas temperature was in equilibrium with the electrode temperature.

9:20am **PS-ThM4 Characterization of the Cold Atmospheric Plasma Hybrid Source***, L. Bardos, **H. Barankova,*** Uppsala University, Sweden

Parameters of the Hybrid Hollow Electrode Activated Discharge (H-HEAD) source for cold atmospheric plasma applications will be described. 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 nozzle by pulsed DC power. The source is capable to produce over 15 centimeters long plasma plume at less than 500 sccm of the argon flow in open air and the microwave power of 500 W (2.4 GHz). Parameters of the hybrid plasma are controlled by both the microwave power and the power delivered to the hollow cathode. An anomalous effect of local maximum in the length of plasma plume at low gas flows is described. Results of the optical emission spectroscopy in argon and neon and electrical parameters of the hybrid discharge will be presented.

9:40am **PS-ThM5 Diagnostics of High Pressure DC Helium Microplasma Discharge***, **Q. Wang**,* University of Houston*; I. Koleva,* University of Sofia, Belgium*; D.J. Economou, V.M. Donnelly,* University of Houston

Gas and plasma diagnostics were performed in a slot-type DC microplasma (200 microns gap) discharge at high pressures. The gas temperature in a helium discharge was estimated by adding small quantities of nitrogen (<100 ppm) into the gas feed. Specific vibrational bands (v'v"), namely (1,3), (0,2) and (1,4) of the N@sub 2@ second positive system, were carefully selected to avoid interference with emission from He atoms and He@sub 2@ excimer. At 250 Torr pressure and 200 mA/cm@super 2@ current density, the gas temperature was T@sub g@ = 350 ± 25 K. The measured gas temperature was almost independent (to within experimental uncertainty) of pressure (in the range of 150 Torr - 600 Torr), and current density (in the range of 100 mA/cm@super 2@ - 400 mA/cm@super 2@). These measurements were consistent with a simplified heat transfer model. Spatially resolved measurements of electron temperature were also performed using trace rare gas optical emission spectroscopy (TRG-OES). These measurements are greatly complicated by collisional quenching at the high operating pressures. Electron density and electron temperature profiles was deduced by comparing emission intensities from the Paschen 2p@sub x@ (x = 1-10) manifold of Ne, Ar, Kr and Xe trace gases. Results suggest that the electron temperature peaks in the cathode sheath region, while the plasma density peaks away from the cathode sheath. A self-consistent fluid model of a DC helium microdischarge was in agreement with the experimental data. Work supported by DOE/NSF.

10:00am **PS-ThM6 Atmospheric-pressure Microdischarges as Short-residence Time Reactors for Silicon Nanoparticle Synthesis***, **R.M. Sankaran**[1], D. Holunga, R.C. Flagan, K.P. Giapis,* California Institute of Technology

Microdischarges are investigated as short-residence time reactors for the synthesis of nanoparticles. The application is attractive since nucleation and growth can be limited in the reaction zone, while charging of particles in the plasma may reduce coagulation downstream. We report here on the gas-phase synthesis of silicon nanoparticles in an atmospheric-pressure dc microdischarge. The discharges are formed in silane/argon gas mixtures between a metal capillary tube (d=180 microns) that serves as the cathode and an anode tube of larger size. Incorporation of gas flow through the discharge results in a continuous production of aerosol particles which are size classified in situ using a radial differential mobility analyzer (RDMA). Based on their electrical mobility, the particles were found to possess relatively narrow distributions (@sigma@@sub g@=1.3-1.5) with mean sizes between 2 and 5 nm depending on reactor conditions. Electrical measurements after synthesis in the microreactor show that the particles are charged both negatively and positively. To further characterize the particles, the aerosol stream is bubbled into solvents directly after synthesis in the microreactor. These colloidal dispersions exhibit strong blue photoluminescence with maximum intensity at 440 nm (2.8 eV). Atomic force microscopy on solutions drop cast on silicon substrates have verified that the particles are as small as 2 nm. In this talk, we will discuss features of this new synthesis technique including effects of discharge conditions on particle growth and optical properties.

10:20am **PS-ThM7 Comparison of Atmospheric Pressure Helium Plasmas Operating in the Abnormal Glow and Recovery Modes***, R.F. Hicks, **X. Yang**[2], M. Moravej, G. Nowling,* University of California, Los Angeles*; S. Babayan, J. Penelon,* Surfx Technologies

The properties of a radio-frequency atmospheric pressure plasma fed with helium and nitrogen were investigated. Two discharge modes were identified with current-voltage measurements and optical emission spectroscopy. After the discharge was struck, the plasma entered an abnormal glow regime with a maximum power density of 4.8 W/cm@super 2@, corresponding to a current density and voltage of 0.73 A/cm@super 2@ and 317 V. Further increasing the power caused the plasma to shift into a new "recovery" mode with a dramatic reduction of current and voltage and a surge in power to 416 W/cm@super 2@. This transition is attributed to sheath breakdown. The spatial emission intensity between the electrodes in the abnormal glow reached a maximum 0.25 mm away from the electrodes. In contrast, the recovery mode exhibited maximum emission intensity at the edge of the electrodes, with an intensity 200 times higher than that of the abnormal glow. The neutral gas temperature measured in the abnormal and recovery modes equaled 75 and 250 °C, respectively. The density of nitrogen atoms produced in the plasma was determined by measuring the temporal decay rate of the first-positive emission of nitrogen molecules, i.e., N@sub 2@(B) @super __@> N@sub 2@(A) + h@nu@. It was found that with 0.4 vol.% N@sub 2@, the abnormal and recovery modes produced 1.0x10@super 16@ and 1.7x10@super 16@ cm@super -3@ N atoms at maximum power densities of 4.8 and 416 W/cm@super 2@, respectively. These results indicate that the abnormal glow is more efficient at dissociating molecules into reactive species. A thorough discussion of the physics and chemistry of the atmospheric pressure plasma will be provided at the meeting.

10:40am **PS-ThM8 Atmospheric He-O@sub 2@ DBD Plasma for Steel Decontamination***, **E. Michel**,* Universite Libre de Bruxelles, Belgium*; E. Silberberg,* Arcelor Group*; F. Reniers,* Universite Libre de Bruxelles, Belgium

The use of a DBDs allows the stabilization of cold plasmas at atmospheric pressure which are of a great interest for industrial surface treatments because they do not request expensive vacuum systems. Contrary to wet treatments traditionally used to clean steel surfaces, the plasma treatments are environmental friendly, as they do not produce toxic waste.

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

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

Standard steel surfaces were covered with various amounts of oil using dip coating. The contaminated surfaces were treated using atmospheric pressure plasma in a DBD. In our configuration, the hot electrode only is covered with the dielectric, whereas the other electrode being the sample. Voltages between 1 to 4 kV were applied between the electrodes, at a frequency varying between 5 and 30 kHz. The plasma gas consisted in a mixture of He-O@sub 2@ (2 to 10 % oxygen), at atmospheric pressure. The plasma chemistry was characterized using optical emission spectrometry (OES). The electrical characteristic of the plasma were recorded as a function of the applied voltage, frequency and gas composition. The transition parameters between the homogenous glow discharge and the filamentary one were established for our configuration. The kinetics of decontamination was studied by Auger electron spectroscopy (AES) and infrared spectroscopy (IRRAS- FTIR). The effect of the frequency, the applied voltage, the discharge current, the initial amount of contamination and the plasma gas composition on the kinetics of oil degradation was studied and discussed. The resulting surface state of steel was investigated using AES and X-ray photoelectron spectroscopy. Finally, a macroscopic model for the kinetics of decontamination of steel surfaces by He-O@sub 2@ atmospheric plasmas is proposed.

11:00am **PS-ThM9 Line Plasma Generation of Microwave Employing Narrow Width Waveguide**, *T. Fukasawa,* Tokai University, Japan*; S. Fujii,* ADTEC Plasma Technology Co., Ltd., Japan*; **H. Shindo**,* Tokai University, Japan

Line plasma over 40 cm in length has been required for large area plasma processing at relatively higher pressure or atmospheric pressure. The line plasma will be applied to surface treatment of rolled organic thin film; furthermore, processing of large area flat panel such as large area LCD. The width of conventional rectangular waveguide is about 10 cm, therefore wavelength(@lambda@g) in the waveguide is about 15cm. However, the @lambda@g is increased with the decrease of the width of the waveguide. @lambda@g = @lambda@/@sr@(1-@lambda@/2W)@super 2@. @lambda@ is wave length in free space and W is width of the waveguide. We manufactured very narrow rectangular waveguide, whose inner widths are 63.5mm, 61.8mm and 61.5mm, respectively. Length and inner thickness of the waveguide are 500mm and 5mm respectively. 2.45 GHz microwave was introduced to the narrow waveguide through TE mode rectangular waveguide (BRJ-2), three-stub tuner and rectangular tapered waveguide. Electric field in the narrow waveguide was measured using electric probe. Measured @lambda@g was corresponded to the above-mentioned formula. @lambda@g was over 1m at the waveguide width of 61.5mm. A slit was made on the side of the wave-guide of 400mm in length and 1mm in width. A quartz tube was set on the slit, whose inner diameter and outer diameter were 3mm and 4mm, respectively. Length of the quartz tube was 400mm. He gas was introduced into the quartz tube. Pressure was measured by capacitance manometer. At the microwave power of 200W, some sections were observed corresponding to wavelength of microwave in free space. At the microwave power of 1kW, however, uniform optical emission intensity was achieved. Optical emission spectrum (OES) intensity at the wavelength of 656nm was measured in order to measure the distribution of electron density in the quartz tube. At the microwave power of 1kW, uniformity of the OES intensity was +-8.4%.

11:40am **PS-ThM11 Atmospheric Pressure Plasma Liquid Deposition - A New Route to High Performance Coatings**, ***S.R. Leadley**, L. O'Neill, L.-A. O'Hare, A.J. Goodwin,* Dow Corning Ltd., Ireland

Plasma enhanced coating processes are well known as a route to well adhered, conformal, high performance coatings. Dow Corning Plasma Solutions has developed a new coatings approach, which was invented in collaboration with the Department of Chemistry of the University of Durham, UK. Atmospheric Pressure Plasma Liquid Deposition combines atmospheric pressure glow discharge (APGD) technology with a unique precursor delivery system. This process operates at atmospheric pressure and ambient temperature allowing the use of a wide range of liquid precursors. The plasma causes polymerization of the precursor so that it is deposited as a conformal, well-adhered thin-film coating, which retains all the functionality and value of the original liquid monomer precursor. This technology retains flexibility with respect to process chemistry and the capability to deliver a vast range of surface functions through the mixing and matching of precursors. The aim of this presentation is to introduce the technology behind this new process and show examples of coatings that have been prepared using mixed monomers, so that the properties of the coating can be tailored.

Semiconductors

Room 304B - Session SC+EM-ThM

Wide Bandgap Semiconductors

Moderator: D.D. Koleske, Sandia National Laboratories

8:20am **SC+EM-ThM1 HVP-CVD: A Novel Chemical Vapor Deposition Approach for Zinc Oxide Synthesis**, ***T.M. Barnes**, J. Leaf, C. Fry, C.A. Wolden,* Colorado School of Mines

Zinc oxide (ZnO) is a versatile II-VI semiconductor that has generated tremendous interest due to its unique combination of optical, electronic and mechanical properties. High vacuum plasma-assisted chemical vapor deposition (HVP-CVD) is introduced as a novel technique for the deposition of zinc oxide and the study of the associated surface chemistry. An inductively coupled plasma (ICP) source was used for the generation of atomic oxygen and other radicals. Radicals from the ICP source and organometallic precursors diffuse into a high vacuum environment where they combine to form metal oxide thin films on a heated substrate. The process is differentiated from conventional CVD approaches in that the collisionless environment precludes gas-phase reactions with the metal precursor. Advantages of the HVP-CVD approach were demonstrated for zinc oxide growth using dimethyl zinc. Notable achievements include high growth rates of highly oriented material, room temperature formation of (002)oriented ZnO, and nitrogen doping. The underlying process chemistry was investigated using a combination of in-situ diagnostics and ex-situ materials characterization. Optical emission spectroscopy (OES) and quadrupole mass spectrometry (QMS) were used to monitor the ICP source and deposition environment, respectively. In the case of intrinsic ZnO, the growth kinetics were found to be first order in dimethyl zinc and zero order in atomic oxygen. QMS analysis suggests that growth proceeds through an elegant pathway in which the methyl ligands simply desorb without oxidation. Nitrogen doping was achieved by replacing oxygen with N@sub 2@O in the ICP source. The mechanism of nitrogen incorporation is discussed in light of film properties and characterization of the deposition environment.

8:40am **SC+EM-ThM2 Realization of Mg(x=0.15)Zn(1-x=0.85)O based Metal-Semiconductor-Metal UV Detector on Quartz and Sapphire**, *S. Hullavarad,* University of Maryland*; **R. Vispute**,* Bluewave Semiconductors, Inc.*; T. Venkatesan, S. Dhar, I. Takeuchi,* University of Maryland

MgZnO is a novel oxide based UV sensitive material. The band gap of MgxZn1-xO can be tuned by varying the composition of Mg to achieve band gaps corresponding to UV-A, UV-B, UV-C regions of UV spectrum. This material is of significant importance for various applications in flame sensors, UV index monitors and missile plume detection. The interesting property that makes this material unique is its existence in multiple phases for different Mg compositions. This allows picking up desired Mg composition corresponding to suitable UV sensitive window and growing on lattice matched substrate. In this paper we present the growth of MgZnO on non-conventional substrates like quartz and on sapphire for comparison of the device reliability. MgZnO films are characterized by X-Ray Diffraction, UV-Visible spectroscopy and Rutherford Back Scattering - channeling techniques. We are reporting for the first time the highly oriented growth of MgZnO on quartz by Pulsed Laser Deposition technique with a RBS channeling yield of 50% showing highly ordering. The morphology of the films is studied by Atomic Force Microscopy. The metal-semiconductor-metal device was fabricated on the MgZnO film to study the device response under proper UV irradiation.

9:00am **SC+EM-ThM3 A Non-Traditional Approach to Low-Temperature Nitride Thin Film Deposition and Nanoscale Device Fabrication**, ***M.A. Hoffbauer**, A.H. Mueller, E.A. Akhadov, M.A. Petruska, V.I. Klimov,* Los Alamos National Laboratory **INVITED**

Using energetic neutral atoms to control interfacial chemistry opens new opportunities for low temperature materials processing and device fabrication at the nanoscale. We are developing a unique low-temperature thin film growth and etching technology, exclusive to LANL, called Energetic Neutral Atom Beam Lithography/Epitaxy (ENABLE) that utilizes neutral reactive atomic species (e.g. N and O) with kinetic energies comparable to chemical bonds strengths (a few eV) for growing nitride and oxide thin films at low temperatures and for etching very high-aspect-ratio features into polymers. Co-depositing metals onto substrates simultaneously exposed to energetic N-atoms permits device quality GaN-based semiconducting films to be grown at temperatures ranging from ambient to greater than 500 C on a variety of substrates (including plastics). Characterization details regarding film crystallinity, epitaxy, stoichiometry, and optical properties will be discussed. Low-temperature GaN film deposition permits semiconducting nanocrystals (NCs) synthesized by colloidal chemistry and having size-controlled emission wavelengths to be encapsulated in a GaN-based matrix. Devices based on p-i-n structures show direct charge injection and electroluminescence from the NCs. Using energetic oxygen atoms to selectively etch various nanoscale features in polymeric films yields sub-100 nm features with aspect ratios exceeding 35:1. Examples will be shown where ENABLE is used to directly grow patterned nitride thin film structures by combining the capability to etch polymer templates with subsequent low-temperature thin film growth. Future prospects and challenges for low-temperature ENABLE-based nanoscale fabrication along with progress towards an efficient multicolor (white) light source based on a NC LED device will be presented.

9:40am **SC+EM-ThM5 Confined Epitaxial Growth of GaN for Defect Reduction and Device Development***,* ***C.R. Eddy, Jr.****,* *R.T. Holm, R.L. Henry, M.E. Twigg, N.D. Bassim, L.M. Shirey, F.K. Perkins,* Naval Research Laboratory*; M.C. Peckerar,* University of Maryland*; E.J. Cukauskas,* Sachs Freeman Associates

The family of III-V nitride materials has been the subject of many device technology development efforts, including visible and ultraviolet light emitters and detectors and high power rf transistors. Another area of interest is the development of vertically conducting device technologies for power electronics. In such applications it is critical that the threading dislocations inherent in this heteroeptixial materials system (no native substrate) be eliminated, particularly in the active region of the device. These threading dislocations have been identified as sources of leakage currents and premature failure of voltage blocking devices. In this work, an approach to reduce/eliminate vertical threading dislocations is described and initial results presented. The approach involves confined homo- or hetero-epitaxy of GaN materials using sputtered oxide masks to delineate growth regions. Growth is carried out using conventional MOCVD and conditions that inhibit lateral growth over the mask. The resulting confined epitaxial material is terminated with equilibrium crystal facets that form hexagonal mesas. The material contains a reduced dislocation density (approximately one order of magnitude as determined by TEM) compared to the underlying template layer for homoepitaxial growth. This reduction in dislocation density is believed to be the result of reduced strain in the epitaxial volume and the presence of the free surfaces represented by the sidewalls of the mesa. Characterization of pn junction diodes grown in this manner reveals significantly reduced leakage currents in as-grown structures (1 @mu@A/cm@super2@), which can be further reduced with application of passivation coatings. The approach is well suited to the development of distributed diode device technologies appropriate for power device applications. Issues such as doping variations in the confined epitaxial regions and the impact of additional device filtering techniques will also be presented.

10:00am **SC+EM-ThM6 Conductive Atomic Force Microscopy Studies of Forward and Reverse Current Conduction in GaN Films***,* ***A.A. Baski****,* *J. Spradlin, S. Dogan, H. Morkoc,* Virginia Commonwealth University

We have investigated the current conduction of homo- and heteroepitaxial GaN-based films using conductive atomic force microscopy (C-AFM). For the case of a homoepitaxial film grown by MBE on HVPE template, C-AFM shows premature current breakdown at the centers of hillocks associated with screw dislocations, consistent with the results of other groups. Local C-AFM current-voltage curves of such dislocations indicate a Frenkel-Poole mechanism for forward conduction on defective regions, as opposed to field emission on non-defective regions. In the case of heteroepitaxial GaN films grown on sapphire, C-AFM data do not show a straightforward correlation between topography and current conduction. We observe, however, that films with more rectifying Schottky behavior via standard I-V measurements produce forward and reverse bias C-AFM images with strong asymmetry. In addition, standard I-V data indicate a field emission (forward bias) or hopping (reverse bias) mechanism for a high quality rectifying film, and a Frenkel-Poole mechanism for a lower quality film. This behavior is consistent with the C-AFM I-V data of defective regions on the homoepitaxial film, which also show Frenkel-Poole conduction in forward bias.

10:20am **SC+EM-ThM7 Thin-Film Diamond Electronics: Progress and Expectations***,* ***J.E. Gerbi****,* Argonne National Laboratory **INVITED**

Diamond has long been thought to have the potential to revolutionize electronics due to its exceptional single-crystal properties, including extremely high thermal conductivities and carrier mobilities. Unfortunately, major roadblocks exist for both the growth of affordable single-crystal diamond, and especially for the doping of such material. Non-single crystal diamond, while suffering the degradation of some important single crystal diamond properties, does nevertheless show promise as an extremely useful electronic material. A review of such materials will be given, with emphasis on how the structure of various types of polycrystalline diamond affects key electronic properties. The ability to dope polycrystalline diamond in non-traditional ways will be discussed, as will the integration of diamond thin films in a device environment. Finally, prototype room-temperature device fabrication and performance will be discussed. The emphasis will be made that the field of diamond electronics continues to make significant progress, especially for niche applications such as MEMS and chemical sensors. This work was supported by the DOE-Office of Science-Materials Science under Contract No. W-31-109-ENG-38.

11:00am **SC+EM-ThM9 X-ray Absorption and Emission Studies of Diamond Nanoparticles***,* *T. van Buuren,* Lawrence Livermore National Laboratory*; C. Bostedt,* HASYLAB at DESY, Hamburg, Germany*;* ***T.M. Willey****,* *R.W. Meulenberg,* Lawrence Livermore National Laboratory*; J.Y. Raty,* University of Liege, Belgium*; G. Galli, L.J. Terminello,* Lawrence Livermore National Laboratory

Carbon nanoparticles, produced in detonations, are found to have a core of diamond with a coating fullerene-like carbon. X-ray diffraction and TEM show that the nanodiamonds are crystalline and approximately 4 nm in diameter. These nano-sized diamonds do not display the charateristic property of other group IV nanoparticles: a strong widening of the energy gap between the conduction and valence bands owing to quantum-confinement effects. For nano-sized diamond with a size distribution of 4 nm, there is no shift of the band energies relative to bulk diamond@footnote 1@. The C 1s core exciton feature clearly observed in the K-edge absorption of bulk diamond is attenuated and broadened in the nanodiamond case due to increased overlap of the excited electron with the core hole in the small particle. Also the depth of the second gap in the nanodiamond spectra is shallower than that of bulk diamond. A feature at lower energy in the X-ray absorption spectra that is not present in the bulk samples is consistent with a fullerene like surface reconstruction. By exposing the diamond nanoparticles to an Argon / Oxygen plasma then annealing in a UHV environment, we have obtained a hydrogen free surface. The nanodiamonds processed in this manner show an increase fullerene type contribution in the carbon x-ray absorption pre-edge. High spatial resolution EELS measurements of the empty states of a single nanodiamond particle acquired with a filed emission TEM also show the core of the particle is bulk diamond like whereas the surface has a fullerene like structure. Density-functional theory calculations on clusters show an increase in bandgap only for clusters smaller than 1 nm, and confirm the fullerene-like surface reconstruction. @FootnoteText@ This work is supported by the U.S. DOE, BES Materials Sciences under contract W-7405-ENG-48, LLNL.@footnote 1@ J. Y. Raty, G. Galli, C. Bostedt, T. van Buuren, L. J. Terminello, Phys. Rev. Lett. 90, p.401 (2003) .

11:20am **SC+EM-ThM10 Direct Electronic Sensing of Biological Binding Events on Diamond Thin Films***,* ***W. Yang****,* University of Wisconsin-Madison*; J.E. Butler, J.N. Russell, Jr.,* Naval Research Laboratory*; R.J. Hamers,* University of Wisconsin-Madison

The chemical and physical inertness of diamond combined with its semiconducting electrical properties make it an attractive substrate for biological sensing. We have investigated the direct covalent modification of diamond with a variety of biomolecules including DNA and antibodies, and have investigated the relationships between the interfacial structure and the resulting electrical response observed upon DNA hybridization and antibody-antigen binding. The biological sensitivity and selectivity on diamond surfaces have been optimized using traditional fluorescence methods. By using electrical impedance spectroscopy (EIS), we have been able to detect DNA hybridization and antigen-antibody interactions in real time with high sensitivity. EIS measurements allow us to map out the impedance response as functions of both frequency and potential, helping to separate the electrical properties of the diamond space-charge region, the molecular layers, and the remaining solution. At low frequencies binding can be detected by the ion diffusion through the modified interfacial layers. At higher frequencies binding can be detected through a field effect induced in the diamond. The field effect mechanism allows us to directly detect biological molecules based on the different molecular charges. Complementary measurements on n-type and p-type silicon confirm the overall picture of the transduction process. Our results suggest the possibility of fabricating biological FET devices on diamond thin films.

11:40am **SC+EM-ThM11 Enormous Photocurrent for Hydrogenated Single-crystalline B-doped Diamond Epilayers Grown by Microwave-excited Plasma Chemical Vapor Deposition.***, **Y.K. Koide,*** National Institute for Materials Science (NIMS), Japan

Diamond with energy band-gap of 5.5 eV is an attractive semiconductor for applying to a visible-blind photodetector operated at ultraviolet wavelength smaller than 240 nm. Although there have been several reports for challenges to develop such the photodetector (PD), tremendous efforts were made by applying polycrystalline diamond films to the PDs. Enormous photocurrent (PC), persistent photoconductivity (PPC), and relatively-large thermally-stimulated current (TSC) were reported by several groups to be observed for the polycrystalline diamond DUV-PDs, and the mechanisms of the PPC and TSC were proposed to be due to bulk deep levels, surface states, and/or interface states at grain boundaries in the polycrystalline diamond films. In order to understand the defect-related mechanism of the PPC and TSC, it is required to investigate the photoresponse properties of PD fabricated by single-crystalline diamond epilayer, which will lead to development of high-efficiency diamond DUV-PD with high reliability. Also, it is essential to investigate influences of diamond surfaces terminated by hydrogen and oxygen (named by hydrogenated and oxidized surfaces, respectively) on photoresponse properties, which will provide an important information on effect of surface states on the mechanism of PPC. The purpose of this paper is, as a first step to develop reliable, high-efficiency diamond PD, to explore the PC and PPC for homoepitaxial B-doped diamond epilayer with hydrogenated and oxidized surfaces. The PC's with gain larger than 105 and the long-term PPC were observed in illuminating UV-light to metal/p-diamond/ metal photodiodes fabricated on hydrogenated surfaces of the single-crystalline B-doped p-diamond epilayer. Saturation of PC with increasing applied voltages and phototransistor action against incident optical power densities were observed. The PC with large gain and the PPC were believed to be due to surface states on hydrogenated surface.

Surface Science
Room 210B - Session SS1-ThM

Metal Oxide and Clusters III: Supported Cluster Formation and Reactivity

Moderator: G.S. Hwang, The University of Texas at Austin

8:20am **SS1-ThM1 Decomposition of Dimethyl Methylphosphonate on TiO@sub2@(110)-Supported Ni Clusters of Different Sizes***, **D.A. Chen**, S. Ma,* University of South Carolina*; J. Zhou,* Oak Ridge National Laboratory

The thermal decomposition of dimethyl methylphosphonate (DMMP) on Ni clusters deposited on TiO@sub2@(110) has been studied in ultrahigh vacuum by TPD and XPS. Ni cluster sizes were characterized by STM; the small Ni clusters (5.0±0.8 nm diameter, 0.9±0.2 nm height) were deposited at room temperature while the large clusters (8.8±1.4 nm diameter, 2.3±0.5 nm height) were prepared by room temperature deposition followed by annealing to 850 K. TPD experiments show that CO and H@sub2@ were the major gaseous products evolved from the decomposition of DMMP, and molecular DMMP and methane desorption were also observed. The product yields for CO and H@sub2@ were higher for reaction on the small Ni clusters. Furthermore, XPS experiments demonstrate that the small Ni surfaces decompose a greater fraction of DMMP at room temperature. The loss of activity for the large annealed clusters is not caused by a reduction in surface area, which does not change substantially before and after annealing. Since CO adsorption studies suggest that the loss of activity cannot be completely due to a decrease in surface defects upon annealing, we propose that a TiO@subx@ moiety is responsible for blocking active sites on the annealed Ni surfaces. Low ion scattering studies show that the Ni clusters are not completely encapsulated after heating to 850 K, but these experiments are also consistent with partial encapsulation. Although DMMP decomposes on TiO@sub2@ to produce gaseous methyl radicals, methane and H@sub2@, the activity of the substrate surface itself appears to be quenched in the presence of the Ni clusters. However, the TiO@sub2@ support plays a significant role in providing a source of oxygen for the recombination of atomic carbon on Ni to form CO, which desorbs above 800 K.

8:40am **SS1-ThM2 Nucleation and Growth of 1B Metals on Rutile TiO2(110): Role of Oxygen Vacancies***, **D. Pillay**, G.S. Hwang,* The University of Texas at Austin

Oxide supported metal nanoparticles exhibit distinctly different chemical and physical properties from their bulk counter parts. The unique properties are greatly determined by their size and shape. Tailoring the structural properties with atomic scale precision will therefore offer great opportunities to open up a range of novel chemical, biological, and electronic applications. Due to the complexity of oxide-metal interactions, many fundamental aspects of metal particle nucleation and growth on an oxide are not well understood. We have investigated the nucleation and growth of 1B metals (Cu, Ag, Au) on a rutile TiO2(110) surface using density functional theory slab calculations. Our results clearly demonstrate that Au shows a distinctly different growth behavior from Ag and Cu. In this talk, we will present i) diffusion, nucleation, and early stage of growth of 1B metals on reduced TiO2(110) and ii) role of oxygen vacancies in the metal particle growth. Also, we will discuss the underlying reasons for sintering enhancement upon O2 exposure.

9:00am **SS1-ThM3 Cluster Size and Support Effects on Activity in Supported Gold and Iridium Catalysts***, S. Lee, C. Fan, T. Wu, W. Kaden, **S.L. Anderson**,* University of Utah **INVITED**

Size-selected model catalysts are prepared by deposition of mass-selected gold and iridium cluster ions on single crystal TiO@sub 2@ and thin film Al@sub2@O@sub 3@. Physical properties and adsorbate binding to the resulting samples is probed by a combination of XPS and ion-scattering (ISS). Chemical activity is probed by a combination of temperature-programmed desorption and constant temperature pulse dosing mass spectrometry. CO oxidation on Au@sub n@/TiO@sub 2@ is found to be very strongly dependent on deposited cluster size, with activity turning on at Au@sub 3@, and varying with size for larger clusters. The activity appears to be correlated with changes in the binding of CO from atop gold to peripheral sites associated with the clusters. Comparison of samples prepared by deposition over a wide temperature range suggests that substantial sintering occurs only at temperatures well above room temperaure. Reactions of hydrazine and ammonia on Ir@sub n@/Al@sub2@O@sub 3@, and sintering behavior in this system will also be discussed.

9:40am **SS1-ThM5 Fullerene Surfaces as Templates for Cluster Formation: The Interaction with Silicon and Gold***, **P. Reinke,*** University of Virginia*; H. Kroeger,* Universitaet Goettingen, Germany*; M. Buettner, P. Oelhafen,* Universitaet Basel, Switzerland

Clusters made from different elements are envisaged as building blocks for nanoelectronic devices. The properties of small clusters (@<@100 atoms) exhibit a strong size dependence which allows to tune their properties but places considerable demands on the synthesis of size-selected cluster arrays. The present investigation explores a novel path to the synthesis of size-selected clusters exploiting the strong corrugation and wide range of adsorption sites on the C@sub 60@ surface. Si and Au are the first elements investigated and the possibility to form arrays and network structures will be explored in the future. Amorphous Si (a-Si) and Au were deposited on a fullerene surface and the sequential evolution of the surface and the electronic properties of the interface were observed in-situ by photoelectron spectroscopy (PES) in the ultraviolet and x-ray regime. The growth of the Si on the C@sub 60@ surface begins with the formation of clusters, and analysis of the Si2p core level indicates that they are surrounded by carbon atoms and located interstitially between the C@sub 60@ molecules. As the growth continues the clusters coalesce and an a-Si overlayer forms. The interface contains no SiC covalent bonds and the electronic properties of this sharp interface are determined from the PES data. In contrast, the growth of the Au overlayer begins with the formation of islands, followed by a Vollmer-Weber type growth. The analysis of the core level and valence band spectra yields a wealth of information on the cluster size, electronic structure of the clusters and the interface. A model to describe this behavior will be discussed with special attention to the suitability of the system for cluster array and network formation, and with respect to the future use of highly corrugated surfaces of macromolecule solids to aid these self organization processes.

10:20am **SS1-ThM7 The Role of Defects in the Nucleation, Structure, and Stability of Gold Clusters on Titania***, **W.T. Wallace**, M.-S. Chen, B.K. Min, K.K. Gath, D.W. Goodman,* Texas A&M University

The discovery that Au clusters dispersed on certain metal oxides are efficient catalysts for a variety of low-temperature reactions has stimulated extensive study with the goal of developing a new generation of superior, Au-based catalysts. In this study, the interaction of Au with titania, a commonly used industrial support, has been addressed. Titania, as a 3-D cluster, or a titanium cation, introduced as a heterogeneous defect into a silica thin film, acts as a nucleation site for Au clusters, leading to an enhanced cluster density. Furthermore, both types of defects inhibit Au cluster sintering under reaction pressures and temperatures, thereby circumventing a serious limitation of the typical nanostructured Au catalysts. The growth mode of Au deposited onto titania thin films grown on Mo(112) illustrates the crucial role of surface structure on the Au morphology. On titania films grown on Mo(100), Au forms 3-D clusters when annealed, whereas on a highly defective titania surface grown on Mo(112), Au grows layer-by-layer, forming a thin, ordered film that exhibits exceptional catalytic activity toward CO oxidation.

10:40am **SS1-ThM8 Interaction of CO, Au, and O on Ru(0001)*, Q. Wu*,** *J. Hrbek,* Brookhaven National Laboratory

The coadsorption of O, Au, and CO is studied on the Ru(0001) surface using temperature programmed desorption, Auger electron spectroscopy, and low energy electron diffraction. For low oxygen coverage (O(2x1) or @theta@@sub O@ = 0.5 ML), Au is found to compress the surface oxygen, and contributes to two first-order-like desorption peaks of O@sub 2@ (e.g. ~1150K and ~1200K). The double-peak structure of O@sub 2@ desorption is also observed when Au compresses the "O-rich" Ru(0001) surface (O(1x1) or @theta@@sub O@ ~1 ML excluding subsurface oxygen); the desorption of subsurface oxygen occurs at ~1050K. Desorption is a dynamic process: after subsurface O desorption, compressed surface oxygen starts to desorb and gold spreads on the Ru surface. Au desorption (0.5 ML to 5 ML) from the oxygen modified Ru surface (both O(2x1) and O(1x1)) is consistent with the presence of 3D Au islands. The majority of CO coadsorbed on Au/O/Ru(0001) surface desorbs at low temperatures around 200K; a small fraction reacts with the compressed oxygen to form CO@sub 2@ that desorbs at ~300K.

11:00am **SS1-ThM9 Adsorption and Desorption of Propylene and Ethylene on Au/TiO@SUB 2@*, Y. Yang*,** *M.M. Sushchikh, E.W. McFarland,* University of California, Santa Barbara

TiO@sub 2@ supported Au nanoclusters are of interest both as olefin epoxidation catalysts as well as a more general high activity partial oxidation platform. Four different TiO@sub 2@ (110) surfaces were prepared; ideal, fully oxidized, and defected by 0.1% , 1% and 10% surface area sputtering. Identical exposures (270 K (1%) and 300 K (10%)) while the TiO@sub 2@ related peak remains at 150 K. We propose that Au deposited on a sputtered surface is immobilized at defect sites and that with increased sputtering time there is a decrease in the cluster size. The propylene metal interaction is increased in energy as the cluster size decreases. Similar behavior is observed with ethylene desorption.

11:20am **SS1-ThM10 Chemistry of Sulfur Compounds on Au(111)-Supported Mo Nanoparticles.*, D.V. Potapenko,*** Brookhaven National Laboratory*; J.M. Horn, M.G. White,* BNL and SUNY at Stony Brook

We are using the reconstructed (21 x @sr@3)-Au(111) surface as a template and inert support for depositing Mo nanoparticles for subsequent reactivity studies of desulfurization and the formation of Mo sulfide nanoparticles. Bulk molybdenum sulfide is the basis for commercial hydrodesulfurization (HDS) catalysts and this work is focused on exploring the modification of activity for nanostructured Mo and molybdenum sulfide on various supports. Nanoparticles of Mo were prepared on the Au(111) substrate by two methods: physical vapor deposition of Mo and chemical vapor deposition through the Mo(CO)@sub 6@ precursor. STM studies have shown that Mo nanoparticles are thermodynamically unstable on the Au(111) surface and that gold encapsulates Mo at temperatures > 300 K. It follows from TPD/AES experiments that bare Mo nanoparticles are very reactive: they cause complete dissociation of all the S-containing compounds tried and H@sub 2@ was the only major desorption product observed. Au-encapsulated Mo nanoparticles, on the other hand, are much less reactive. They do not chemically interact with thiophene (C@sub 4@H@sub 4@S). Surprisingly, Au-encapsulated Mo nanoparticles react with both H@sub 2@S and CH@sub 3@SH. The latter compound in this case dissociates only partially, causing S deposition and desorption of CH@sub 4@. We believe that interaction of X-SH compounds with Au-encapsulated Mo nanoparticles proceeds through intermediacy of surface gold thiolates.

11:40am **SS1-ThM11 Metal Oxide Nanowires: How Nano-Electronics Can Contribute to Catalysis*, A.A. Kolmakov*,** *Y. Lilach, M. Moskovits,* University of California, Santa Barbara

We tested the performance of individual metal oxide single crystal nanowires and nanobelts as catalysts and gas sensors operating in high vacuum and under "real world" reaction conditions. We showed that when nanowire radius is comparable with its Debye length, the adsorption/desorption of donor/acceptor molecules on the surface of the nanowire alters the bulk electron density inside the nanowire what can be sensitively monitored via changes in the conductivity of the nanowire. When nanowire is configured as a field effect transistor the availability of free electrons in the bulk for redox surface reactions can be controlled by the gate thus reactivity (sensitivity) and selectivity of the nanowire surface can be tuned electronically. In vivo conductometric measurements on individual nanowire during its surface doping with catalytic particles manifest the drastic enhance of the reactivity/selectivity of this catalyst (sensor) due to selective adsorption and spillover effect.

Surface Science

Room 210C - Session SS2-ThM

Tribology, Adhesion, and Friction

Moderator: I.L. Singer, Naval Research Laboratory

8:40am **SS2-ThM2 Advanced Adhesion Test Methods for Semiconductor Interconnect Film*, A.K. Sikder*,** *N. Gitis, M. Vinogradov,* Center for Tribology, Inc.

For faster signal propagation in integrated circuits, new materials with lower dielectric constant (low-k) values are required with copper metal lines. Low-k materials possess many challenges due to their poor mechanical integrity and weak adhesion to other interconnects, so it is important to characterize their adhesion behavior. There are numerous techniques known for adhesion and delamination testing of coatings, some of the most common being a tape test, stud-pull test, scratch test and an indentation test. Each of them has its advantages, but neither one is universally effective for soft to hard, ultra-thin to thick films. The new testing technology, based on multiple sensors coupled with servo-control of forces and displacements, has been developed to fill this void. A novel technology for scratch testing has been developed in order to evaluate the tribo-mechanical behavior of interconnect thin films, where an indenter moves in both vertical (loading) and horizontal (sliding) directions, while acoustic emission and electrical resistance sensors allow for detection of the initiation of fracture, and the scratch pattern indicates the type of failure. The impression left by scratch testing is then observed using scanning probe and optical microscopy, integrated into the instrument mod. UNMT. Scratch testing on various interconnect blanket and patterned, single and multilayered, polished and unpolished film is presented. Adhesion and delamination characteristics are discussed with respect to the intrinsic properties of the different interconnect films (low-k, copper and tantalum) and their surface roughness. Their effective testing in the stack of the films is complimented by frictional and acoustic measurements. The multi-sensing technology allowed for comprehensive characterization of the scratch, adhesion and durability of thin coatings.

9:00am **SS2-ThM3 Light vs. Heavy Diamond: an Investigation of the Fundamental Origins of Friction*, R.J. Cannara*,** *R.W. Carpick,* University of Wisconsin-Madison

Mechanisms of friction include wear, bond-breaking and surface chemistry, molecular deformation, electronic dissipation, and vibrational excitations (or phonons). Resolving the individual contribution of each of these mechanisms poses a great challenge. To overcome this obstacle and isolate the role of phonons in frictional energy dissipation, we compare insulating crystals that are identical, except for having different isotopic concentration. We report adhesion, as well as load- and temperature-dependent nano-scale friction measurements, for a tungsten carbide-coated Si tip on the hydrogen-terminated (111) surfaces of three single-crystal synthetic Type IIa diamonds. Each of the specimens is composed of a different bulk mixture of @super 12@C and @super 13@C. Varying the average mass and isotopic disorder in diamond strongly influences its phonon band structure and thermal properties. For example, previous work has revealed that both phonon lifetimes and thermal diffusivity of diamond increase with isotopic purification. Moreover, its thermal diffusivity is dramatically enhanced at low temperatures (down to ~100 K). All of these phonon properties determine the probability that atomic vibrations (initially created by slip processes during sliding) will reduce frictional energy dissipation by aiding subsequent slip events. We discuss isotope, or phonon, contributions to atomic-scale friction measurements performed in nitrogen and ultra-high vacuum at different temperatures. In addition, we present evidence for structural interfacial effects that lead to negative differential friction behavior.

9:40am **SS2-ThM5 Frictional Forces and Amontons' Law: From the Molecular to the Macroscopic Scale**, ***U. Landman***, *J. Gao, W.D. Luedtke,* Georgia Institute of Technology **INVITED**

Amontons' law, which was already known to Leonardo da Vinci, states that the friction force is directly proportional to the (normal) applied load, with a constant of proportionality - the friction coefficient - that is constant and independent of the contact area, the surface roughness and the sliding velocity. No theory has yet satisfacorily explained this surprisingly general law, all attempts being model or system dependent. On the basis of large-scale molecular dynamics simulations pertaining to lubricated adhesive and non-adhesive junctions, with morphologically rough (as well as crystallographically flat) confining solid surfaces, and in conjunction with recent experiments, we show that the local energy-dissipation mechanisms are not 'mechanical', as assumed in most models, but â?othermodynamicâ?� in nature. We show that a local analysis of the simulation results, based on division of the system into small cells, leads to a natural description in terms of the Weibull distribution. For the dynamic. non-equilibrium, energy-dissipating process that we study, this long-tail distribution serves a similar purpose as the Boltzmann distribution for classical systems at equilibrium. While Amontons' law does not hold on the local scale, it is recovered on the global scale, with the spatio-temporal averaging utilizing the Weibull distribtion of the local friction forces. Interestingly, the concept of "area of contact", often used in frictional studies, does not enter into our analysis. J. Gao, W.D. Luedtke, D. Gourdon, M Ruths, J.N. Israelachvili, U. Landman, Feature Article, in J. Phys. Chem. B 108, 3480 (2004).

10:20am **SS2-ThM7 Activation of SiC Surface for Vapor Phase Lubrication by Chemical Vapor Deposition of Fe**, ***D. Kim***, *A.J. Gellman,* Carnegie Mellon University

Vapor phase lubrication (VPL) has been proposed as a method for lubricating high temperature engines. During VPL, lubricants such as tricresylphosphate (TCP), (CH@sub 3@-C@sub 6@H@sub 4@O)@sub 3@P=O, are delivered through the vapor phase to high temperature engine components where they react to deposit a thin, solid, lubricating film. Although ceramics such as SiC are desirable materials for high temperature applications their surfaces are unreactive for the decomposition of TCP and thus not amenable to vapor phase lubrication. As a means of activating the SiC surface for TCP decomposition we have used chemical vapor deposition of Fe from Fe(CO)@sub 5@. Modification the SiC surface by the presence of Fe accelerates subsequent decomposition of TCP and deposition of P and C on the surface. m-TCP decomposes more readily in the temperature range of 300 K - 500 K on Fe-coated SiC surfaces than on SiC surfaces. The C and P deposition rates depend on the thickness of the Fe film and are further enhanced by oxidation of the Fe. This work provides a proof-of-concept demonstration of the feasibility of using vapor phase to lubricate ceramics.

10:40am **SS2-ThM8 In Situ Studies of Interfacial Rheology of MoS2 and Most Solid Lubricating Coatings**, *G.Y. Lee, I.L. Singer,* Naval Research Laboratory; ***K.J. Wahl,*** Naval Research Laboratory, US

Materials properties (e.g. composition, microstructure, and mechanics) of both solid lubricant coatings and their interfacial transfer films have long been recognized as important to tribological performance. These properties are generally evaluated ex situ, before and after sliding have occurred. However, in situ observations of contacts have shown that interfacial rheology - the deformation and flow of matter within the contact - plays a significant role in controlling friction, wear and endurance of solid lubricants. In this paper, we will present real-time observations of interfacial rheology of MoS2 and MoST@footnote 1@ (Ti-Mo-S) coatings using in situ tribometery. The coatings were deposited by closed field unbalanced magnetron sputtering and contained between 0 and 20% titanium. Reciprocating tests were performed in both dry (<1%) and ambient air (45-60% RH) at 1-4 mm/s and under 1.1 GPa mean contact stress. The interface rheology was studied quantitatively using optical microscopy techniques. Transfer film buildup and depletion were monitored quantitatively using interference fringes, while interfacial dynamics (locus of sliding, stability, and strain rate) were evaluated through video microscopy. The interfacial rheology of MoS2 coatings was strongly influenced by environment (dry vs. humid). In contrast, interfacial rheology of MoST coatings was far less sensitive to humidity, but was strongly influenced by evolution of wear track surface composition and morphology. We will demonstrate how these quantitative measures of interfacial rheology can be used to help us interpret how transfer films influence friction, wear and endurance of MoS2-based solid lubricant coatings. @FootnoteText@ @footnote 1@ D.G. Teer, Wear 251 (2001) 1068-1074.

11:00am **SS2-ThM9 Self-Assembled Monolayers: The Origin of Molecular Level Friction**, ***R.C. Major***, *X.-Y. Zhu,* University of Minnesota; *J.E. Houston,* Sandia National Laboratories

Functionalized self-assembled monolayers (SAMs) are being used in a broad spectrum of disciplines to control the chemical and physical properties of surfaces at the molecular level. Despite a large number of studies, current understanding of the mechanical properties of these functional SAMs is rather incomplete. This arises in part because of the difficulty in quantitatively measuring adhesion and friction forces on the molecular level, and due to the non-trivial task of preparing well-ordered, functionalized thiol monolayers containing reactive endgroups (e.g. HS-(CH@sub 2@)@sub n@-COOH vs HS-(CH@sub 2@)@sub n@-CH@sub 3@) on Au(111) substrates; the latter has often been overlooked in the past literature. Here we report a quantitative study on the tribological properties of functionalized SAMs on Au(111) using Interfacial Force Microscopy (IFM). We show the intimate relationship of tribological properties with the chemical state of the SAM. For example, in the case of -COOH terminated SAMs, we observed a dramatic reversible change in friction response corresponding to the protonated and deprotonated state of the -COOH groups. This frictional response showed an interesting dependence on the conformation and length of the alkyl chains. Microscopic models correlating chemical interactions to tribological properties at the interface will be discussed. This work was supported by Sandia National Laboratories a multi-program laboratory operated by Sandia Corporation, a Lockheed Martin company, for the DOE under Contract DE-AC04-94AL85000.

11:20am **SS2-ThM10 Nanotribological Effects of Substrate Surface Order and Partial Fluorination for Alkanephosphonic Acid Self-Assembled Monolayers on Alumina**, ***M.J. Brukman,*** University of Wisconsin-Madison; *T.D. Dunbar,* 3M Company; *R.W. Carpick,* University of Wisconsin-Madison

SAMs are of considerable interest for applications such as lubrication, corrosion protection, and water repellency, particularly at the nano-scale. Here, we compare the wettability and nano-scale friction and adhesion of two phosphonic acid self-assembled monolayers (SAMs): CF@sub 3@(CF@sub 2@)@sub 7@(CH@sub 2@)@sub 11@-PO@sub 3@H@sub 2@ (F8H11 PA) and CH@sub 3@(CH@sub 2@)@sub 17@-PO@sub 3@H@sub 2@ (H18 PA) deposited on a series of three Al@sub 2@O@sub 3@ surfaces: C- and R- plane single crystal sapphire, and an amorphous alumina layer on Si. Contact angle measurements were performed to compare the wetting of fluorinated and hydrogenated SAMs by water and hexadecane. Atomic force microscopy was then used to characterize the nano-scale dependences of adhesion and friction on SAM composition and substrate surface order. We observe differences that depend on the substrate, indicating that substrate-imposed variations in packing density and ordering have measurable nanotribological effects.

11:40am **SS2-ThM11 Tribological Behavior of Self-Assembled Double Layer Measured by a Pin-on-plate Method**, ***M. Nakano***, *T. Ishida, T. Numata, Y. Ando, S. Sasaki,* National Institute of Advanced Industrial Science and Technology, Japan

We investigated the tribological behavior of self-assembled double layers using pin-on-plate method in this study. Previously we have been investigated the tribological behavior of alkanethiol self-assembled monolayers using pin-on-plate method and X-ray photoelectron spectroscopy [1]. We found that the friction coefficient was dependent on the alkylchain length and that even a monolayer film has sufficient durability against friction, although the friction coefficients measured at 0.2-0.3 were slightly high. It was pointed out that formation of a new overlayer on monolayer could lead to decrease the friction. From this point of view, here we investigated the tribological behavior of self-assembled double layers using pin-on-plate method. Double layer preparation on Au substrates was performed in a glass beaker at room temperature. Substrates were first exposed to a 1 mM of mercaptohexadecanoic acid solution in ethanol for 24 h. Then, the samples were exposed to a 1 mM of copper acetate solution in ethanol for approximately 5 min. Finally, the samples were exposed to a 1 mM of octadecanethiol solution in ethanol for 24 h [2]. The frictional properties of the SAMs were examined by a pin-on-plate tribometer with a load of 30 mN and sliding speeds of 1 mm/sec (0.2 Hz). The friction coefficient on double layer was kept at 0.10-0.15 for about 30 min, indicating that the topmost octadecanethiol layer was expected to act as the mobile layer and effective to decrease the friction. Ref. [1] M. Nakano, T. Ishida, T. Numata, Y. Ando, S. Sasaki: Jpn. J. Appl. Phys. 42 (2003) 4735. [2] H. Ohno, L. A. Nagahara, W. Mizutani, J. Takagi, H. Tokumoto: Jpn. J. Appl. Phys. 38 (1999) 180.

Surface Science
Room 213B - Session SS3-ThM

Halogen and Oxygen Surface Reactions and Etching

Moderator: J.J. Boland, Trinity College Dublin, Ireland

8:20am **SS3-ThM1 Ultra-Low Coverage Spontaneous Etching and Hyperthermal Desorption of Aluminum Chlorides from Cl2/Al(111)***, **A.C. Kummel**, T.J. Grassman, G.C. Poon,* University of California, San Diego **INVITED**

Non-resonant multiphoton ionization and time-of-flight mass spectrometry have been used to monitor the desorption of aluminum chloride (AlxCly) etch products from the Al(111) surface at 100 K and 500 K during low-coverage (< 5% monolayer) monoenergetic Cl2 (0.11 eV to 0.65 eV) dosing. The desorption products in this low-coverage range show predominantly hyperthermal exit velocities under all dosing conditions. For example, with 0.27 eV incident Cl2, the etch product was found to have a most-probable velocity of 517 Â± 22 m/s at an Al(111) surface temperature of 100 K. This corresponds to 22 times the expected thermal desorption translational energy for AlCl3. Sticking probability measurements and AlxCly etch rate measurements show etching even at Cl2 coverages of less than 5% monolayer at surface temperatures between 100 K and 500 K. These experimental results are consistent with a combination of fast-time-scale surface agglomeration of the adsorbed chlorine to form aluminum chlorides and the presence of activated aluminum chloride chemisorption states having potential energies above the vacuum level. Density functional theory calculations yield results that are consistent with both our experimental findings and mechanistic descriptions.

9:00am **SS3-ThM3 Real-time and In-situ Surface Stress and STM Measurements and their Application to Halogen Etching of Silicon Surfaces***, **T. Narushima**, N. Kinahan, J.J. Boland,* Trinity College Dublin, Ireland

All reactions between surfaces and other species induce strain at the interface to compensate for size differences, electronegativity differences, morphology changes etc. These days, to understand detailed reaction mechanism, contribution of the strain is an important factor which cannot be ignored. The resolution of SPM, however, is poor for this purpose because it does not have absolute but relative resolution. This makes strain determination via this visual method unreliable. In this presentation, we will demonstrate how this induced strain can be determined more accurately through simultaneous surface stress measurements and STM observations as a function of time. To realise this, we have designed a special monitoring system. Surface stress can be readily measured via a capacitance method. The bending of a simple cantilever was measured as a change of capacitance between sample itself and reference electrode. Change from an initial capacitance value corresponds to sample bending which indicates the surface stress change. For surface structure observation, we used conventional STM. In this configuration, conventional direct current heating of the cantilever Si sample is not possible. To heat and prepare samples we used an infrared heating source. This method allowed us to heat sample via a non-contact and static means, which is preferable for STM observation as it induces no noise effects during imaging. At high temperature, surface stress measurements become quite difficult, because high temperature induces thermal stress at interface between heterogeneous materials of sample holder. To avoid this affect, we chose a good combination of quartz and super invar that both have low thermal expansion coefficients and almost equivalent values. We will describe the application of this system to the study of halogen etching of Si surfaces.

9:20am **SS3-ThM4 Chemically Assisted Ion Beam Etching of GaAs by Argon and Chlorine Gases: Experimental and Simulation Investigations***, **A. Rhallabi**,* University of Nantes, France*; M. Gaillard,* Veeco, France*; L. Elmonser,* IMN-LPCM, France*; G. Marcos,* LPCM-IMN, France*; A. Talneau,* LPN-CNRS, France*; F. Pommereau,* OPTO+, France*; P. Pagnod,* University of Nantes, France*; J.P. Landesman,* LPCM-IMN, France*; N. Bouadma,* France Telecom

It is now evident that the improvement of the optical and electrical performances of the III-V components depends on the optimization of the critical process steps such as the dry etch processes especially for the submicron and nanometer devices. The Chemically Assisted Ion Beam Etching (CAIBE) is one of dry etch processes where etching rate and etched surface profile are controlled by the synergy between the reactive neutral species and ion bombardment. This technique uses inert ion bombardment in a reactive gas environment to achieve a separate control between sputtering and chemical etching components. A direct injection of a reactive gas close to the surface avoids the development of chemical reactions in gas phase and allows to have a better control of the transfer of the slopes in the case of mesa structure etching and the anisotropy in the case of trench etching. Experimental investigations of the chlorine and argon CAIBE process for the fabrication of vertical, ultrahigh quality facets in GaAs are reported. The effects of CAIBE process parameters as ion current and energy, chlorine flow rate and substrate temperature on the etching rate and etched GaAs topography evolution have been analyzed. To complete the experimental study, two types of 2D CAIBE model have been developed to predict the etching rate evolution and the etching GaAs profiles through the mask. The first one is an analytical model based on the concept of adsorbed surface fraction by chlorine and the second is based on the Monte-Carlo technique to study the etched surface kinetic. For both models, the simulation and the experiment results agree well with the experiment. Finally, in order to assess the compliance of Cl2/Ar+ CAIBE etching with device applications, 980 nm Ridge lasers have been processed and their electro-optic characteristics have been compared to regular wet-chemical etched ridge stripe.

9:40am **SS3-ThM5 Semiconductor Surface Chemical Functionalization for Microelectronics Applications: Gas Phase Chlorination of H-Passivated Silicon Surfaces***, **S. Rivillon**, F. Amy, Y.J. Chabal,* Rutgers University*; M.M. Frank,* IBM

Controlling the surface chemistry of semiconductor surfaces is critical and particularly important for the growth of alternative dielectrics (i.e. other than SiO@sub 2@) on silicon surfaces. For high-k dielectrics growth using atomic layer deposition, for instance, the chemical nature of the surface determines the abruptness of the resulting interface. Chlorination of H-terminated surfaces is a powerful way to grow high-k dielectrics with minimum interfacial SiO@sub 2@ and needs to be studied. We used several different processes to chlorinate the surfaces: chlorine Cl@sub 2@ gas phase, wet chemistry and photochlorination, and investigated the resulting surfaces by infrared absorption spectroscopy looking directly at the Si-Cl modes. The surface termination is independent of the chlorination method: 1) H-terminated Si(111) surfaces are fully covered by chlorine and remain atomically flat meaning that chlorination processes do not change the surface morphology; 2) only partial chlorination of the Si(100) surface is achieved, with a high degree of disorder. The stability of both chlorinated surface has been studied under nitrogen (N@sub 2@) and in ambient atmosphere.

10:00am **SS3-ThM6 Charge-Carrier-Stimulated Halogen Desorption from Si(100)-(2x1)***, **B.R. Trenhaile**, G.J. Xu, A. Agrawal, A.W. Signor, K.S. Nakayama, J.H. Weaver,* University of Illinois at Urbana-Champaign

Scanning tunneling microscopy was used to investigate spontaneous Br atom desorption from Br-terminated Si(100)-(2x1) as a function of temperature for 620 â?" 775 K. Significantly, analysis demonstrates that the activation energy and pre-exponential factor for the desorption depend on both the doping type and concentration. Moreover, the kinetic parameters are observed to follow the compensation (Meyer-Neldel) rule, and analysis yields a characteristic energy in good agreement with the phonon Debye energy for silicon. The activation energies correspond to the antibonding Si-Br levels, and we propose that thermally-excited charge carriers produce intermediate electronic states that lead to a novel form of electron-stimulated desorption. The desorption of other halogens from Si(100) will also be discussed.

10:20am **SS3-ThM7 Morphological Evolution during Competitive Etching and Oxidation of Vicinal Si(100) Surfaces*, M.A. Albao*,** *D.-J. Liu, J.W. Evans,* Iowa State University

Exposure of a vicinal Si(100) surface to oxygen at ~600C produces etching-mediated step recession. This process is impacted by the formation oxide islands which act as pinning centers for the receding steps, as observed in STM studies by Pelz et al. We develop an atomistic model for this process which accounts for the interplay between oxygen surface chemistry (adsorption, diffusion, oxide formation, and etching via SiO desorption) and the Si surface and step dynamics (anisotropic diffusion and aggregation of vacancies formed by etching with each other or with steps, and attachment-detachment dynamics at steps incorporating anisotropic energetics). Kinetic Monte Carlo simulation of this model produces etch morphologies where receding steps retain qualitative features of their equilibrium morphology (alternating rough SB steps and smooth SA steps), although pinning greatly distorts equilibrium structure (as seen in STM studies). Even without pinning, step evolution is a driven far-from-equilibrium process (as is step flow during MBE) which is impacted by the details of the etching process (e.g., anisotropic vacancy diffusion can lead to an alternation between etch pit nucleation and step flow on adjacent terraces). Simulations used to characterize the dependence of the complex etch morphologies for this model on temperature and oxygen pressure.

10:40am **SS3-ThM8 Atomic Oxygen Etching of Phosphorous-containing Polymer Surfaces*, H. Fairbrother*,** *G. Wolfe, J. Torres,* Johns Hopkins University

The aerospace industry has recently developed phosphorous-containing polymers that can resist the severely oxidizing environment encountered by vehicles traveling in Low Earth Orbit (LEO). Post-flight analysis shows that upon exposure to atomic oxygen (AO) present in LEO, these polymers form a self-passivating phopshate like (P@sub x@O@sub y@)overlayer that hinders etching of the underlying bulk. The protective capabilities of these phosphorous-containing polymers, whose synthesis is complex and expensive, derive solely from the chemical characteristics of the near surface region rather than the bulk. In an attempt to develop a more cost-effective and generally applicable method of creating polymer surfaces with the ability to resist etching by AO, we have initiated studies on polyethylene (PE) ion-implanted with trimethylphosphine. X-ray photoelectron spectroscopy reveals that under ambient conditions the P-implanted PE readily oxidizes to form phosphate-containing bonds at the surface. The thickness of the phosphate layer increases with a logarithmic dependence on air exposure, indicating that the growing phosphate structure limits diffusion of oxygen species through the near-surface region. Subsequent exposure of these films to AO leads to carbon etching from the surface, leaving behind a phosphorous-rich overlayer. Related studies of thin films used to simulate the P-implanted PE surface show that these phosphate structures remain thermally stable under vacuum conditions up until ~650 K. Results from atomic force microscopy studies will also be presented to illustrate the morphological changes in the polymer surface that accompany air oxidation and AO exposure.

11:00am **SS3-ThM9 Structural Damage of Self-Assembled Monolayers Induced by 5-eV O@super +@ Bombardment*, T.D. Tzvetkov*,** *X. Qin, D.C. Jacobs,* University of Notre Dame

Self-Assembled Monolayers (SAM) of decanethiol/Au(111) are bombarded with 5-eV O@super +@ ions in UHV. XPS reveals that the carbon content of the SAM decreases, while the oxygen content increases with O@super +@ dose. STM images of ion-exposed and unexposed regions of the SAM are compared. The SAM layer exhibits greater disorder after only modest doses of 5-eV O@super +@ ions. Initially, ion-induced damage occurs predominantly near domain boundaries, surface steps, and vacancies. In contrast, large defect-free surface domains show considerable stability against 5-eV O@super +@ bombardment. A mechanism for degradation of the SAM by low-energy O@super +@ ions is proposed.

11:20am **SS3-ThM10 In-situ STM-studies of Solid/Liquid Interfaces:Growth of Ultrathin Compound Films**, *A. Spaenig, S. Huemann, J. Hommrich, P. Broekmann,* ***K. Wandelt,*** University of Bonn, Germany

Electrochemical Atomic Layer Epitaxy (ECALE) is quite an interesting alternative route for the synthesis of ultrathin layers, instead of vacuum based chemical vapour deposition techniques. This technique is based on alternating reductive and oxidative underpotential deposition (UPD) processes, e.g. of metal cations and halide or chalcogenide anions. In this contribution the growth of ultrathin semiconducting cadmium sulfide and insulating cadmium chloride films on Cu(111) and Cu(100) single crystal electrodes has been studied in-situ using an ElectroChemical Scanning Tunnelling Microscope (ECSTM). Atomically resolved ECSTM images are presented and discussed for the binary systems of either sulfide or chloride on Cu(111) and Cu(100) as well as for the ternary systems of cadmium sulfide and cadmium chloride on both surfaces. Chloride forms a (@sr@3 x @sr@3)R30° and c(2x2) adsorbate structures on Cu(111) and Cu(100), respectively, and has only a restructuring influence on the morphology of surface steps. In turn, sulfide forms several structures of low and high commensurability on both Cu surfaces, namely a c(2x6) on Cu(100) and a (@sr@7 x @sr@7)R19.1° and (2@sr@7 x 2@sr@7)R19.1° on Cu(111). Moreover at very positive electrode potentials sulfide induces severe reconstructions of both Cu surfaces with a checker-board like superstructure on Cu(100) and a hexagonal Moire like superstructure on Cu(111). Post-deposition of cadmium onto the chloride or sulfide pre-covered Cu surfaces leads to the formation of cadmium chloride or cadmium sulfide compound layers with interest periodic nanoscale superstructures whose physical properties are further characterized by ex-situ electron and ion spectroscopies.

Thin Films

Room 303C - Session TF-ThM

Modeling & Fundamentals in Thin Film Deposition

Moderator: M.C.M. van de Sanden, Eindhoven University of Technology, The Netherlands

8:20am **TF-ThM1 Evolution of Surface Morphology during Thin Film Growth by Hot-Wire CVD: Short-Range Smoothening and Long-Range Roughening*, B.A. Sperling*,** *J.R. Abelson,* University of Illinois at Urbana-Champaign

During thin film growth by low-pressure chemical vapor deposition, the surface morphology evolves due to a kinetic competition between roughening, driven by self-shadowing or stochastic processes, and smoothening due to surface diffusion. When a very smooth substrate is used, the surface roughness increases only very slowly. A more powerful way to study the surface dynamics is to prepare a substrate with an intentional roughness of ~ 5 nm, then deposit film under "high quality" conditions that favor smoothness, and measure the rapid decrease in surface roughness with increasing film thickness. We use this procedure to study the growth of hydrogenated amorphous silicon by hot-wire chemical vapor deposition. Using in situ spectroscopic ellipsometry, we observe that the surface roughness of the film decreases as it grows. However, post-deposition atomic force microscopy reveals a linear increase in the roughness. We resolve this apparent discrepancy by analyzing the power spectrum densities of the atomic force images, which indicate that the growth surface is experiencing both short-range smoothening and long-range (global) roughening. The ellipsometry data agree semi-quantitatively with the short-range atomic force microscopy data, but due to light scattering they exclude information about the long-range components of roughness. The slope of the power spectrum density (short-range scaling) indicates that surface diffusion is the dominant smoothening mechanism, while the linear increase in roughness is consistent with columnar growth caused by self-shadowing. We also discuss possible means to interpret the rate of smoothening data in terms of the adspecies surface diffusivity during hot-wire chemical vapor deposition.

8:40am **TF-ThM2 Atomic-Scale Analysis of SiH@sub 3@ and H Surface Diffusion on Plasma-Deposited Amorphous Silicon Thin Films**, *M.S. Valipa,* University of California, Santa Barbara*; T. Bakos,* University of Massachusetts, Amherst, usa*; E.S. Aydil,* University of California Santa Barbara*;* ***D. Maroudas,*** University of Massachusetts, Amherst

Hydrogenated amorphous silicon (a-Si:H) thin films grown by plasma-assisted deposition from silane-containing discharges are used widely in the fabrication of solar cells and flat panel displays. Film properties, such as surface roughness and film crystallinity, depend on the mobility of reactive species that impinge on the film surface during deposition. Surface transport of SiH@sub 3@ radicals and H atoms is particularly important in determining film smoothness and affecting film crystallinity, respectively. This presentation focuses on detailed atomic-scale analysis of diffusion of SiH@sub 3@ and H on the a-Si:H surface. Using molecular-dynamics (MD) simulations of repeated impingement of SiH@sub 3@ radicals on the growth surface, we modeled the deposition of a-Si:H films on crystalline Si (c-Si) substrates. MD-grown a-Si:H film surfaces were found to be remarkably smooth due to valley-filling mechanisms mediated by diffusion of SiH@sub 3@, the mobile precursor, and resulting in passivation of dangling bonds present in surface valleys or at valley edges. Surface migration of SiH@sub 3@ is driven by the Si-Si bond strain distribution on the surface, which is strongly coupled with the surface morphology and reactivity. In addition, exposure of MD-grown a-Si:H films to H atoms from an H@sub 2@ plasma leads to formation of nanocrystalline regions in the films. Analysis of MD trajectories revealed that H atoms diffuse on the a-Si:H surface and into the bulk film and insert into strained Si-Si bonds; this leads to local structural relaxation and triggers disorder-to-order transitions. We also report results of first-principles density functional theory (DFT) calculations performed using c-Si surfaces as representative models of atomic bonding at film growth surfaces. The DFT results are consistent with the mechanisms of SiH@sub 3@ and H transport identified by the MD simulations and provide quantitative predictions of the migration energetics.

9:00am **TF-ThM3 Substrate Temperature Dependence of the Roughness Evolution of Hot-wire Deposited a-Si:H Studied by Real-Time Spectroscopic Ellipsometry and Atomic Force Microscopy***, **W.M.M. Kessels**, J.P.M. Hoefnagels, E. Langereis, M.C.M. van de Sanden,* Eindhoven University of Technology, The Netherlands

The growth process of hydrogenated amorphous silicon (a-Si:H) by hot-wire CVD is studied by analyzing the surface roughness evolution during film growth for different substrate temperatures. This analysis gives information on aspects such as nucleation and initial film growth, surface roughening and smoothening, and surface diffusion mechanisms. Purely amorphous films have therefore been deposited at low deposition rates while monitoring the growth by real time spectroscopic ellipsometry for temperatures between 70 and 450 @degree@C. The thickness of the surface roughness is deduced from a two-layer optical model and analyzed as a function of the film thickness. Furthermore, the surface roughness of the as-deposited films has also been analyzed by atomic force microscopy (AFM) yielding information about the lateral scaling of the roughness. The initial film roughness is identical for all substrate temperatures indicating a similar nucleation behavior at the different temperatures. The position of the amorphous-to-amorphous roughening transition is observed within the film thickness range of 10-20 nm while an optimum is found for 250 @degree@C. The final surface roughness at a film thickness of 200 nm decreases up to substrate temperatures of 250 @degree@C after which the surface roughness remains fairly constant. The growth exponent @beta@ deduced from the roughness evolution as a function of deposition time, however, decreases for increasing temperature from ~0.20 at 70 @degree@C to ~0.05 at 450 @degree@C in agreement with the temperature dependence of the roughness exponent @alpha@ deduced from the AFM measurements. This suggests a thermally activated surface diffusion mechanism which will be discussed in detail and the relation between the surface roughness evolution and the a-Si:H film properties will be addressed.

9:20am **TF-ThM4 A Self-Consistent Prediction of a Deposition of Cu Sputtered in a rf Magnetron Plasma***, **T.Y. Yagisawa**, T.M. Mine, S.K. Kuroiwa, T.M. Makabe,* Keio University, Japan

Magnetron sputtering has been widely used for thin film deposition in material processing. Radio frequency magnetron is practically employed in the field of dielectric material sputtering in addition to metal targets. In the rf magnetron sputtering system, neutral transport sputtered from a target is of first importance to deposit uniform film. In this paper, we have performed a self-consistent prediction of an rf magnetron plasma structure, velocity of ions impinging a target surface and its erosion profile, ejection neutral atom from the target, and neutral transport to the substrate by using a hybrid model consisting of PIC/MC model of electrons, RCT model of ions and MCS of sputtered neutrals. Typical example is shown in an rf sputtering of Cu target at 13.56 MHz in Ar at 5 mTorr. It is found that rf magnetron at low power supply is maintained mainly by the electron multiplication at the region where ExB is maximum, and auxiliary by the secondary electrons from the target in the region with ExB=0. The latter mechanism which is completely different from the dc magnetron sputtering will become dominant with increasing the dissipated power. Ion velocity distribution at the target surface shows a strong anisotropy due to low pressure and radial dependence. Flux and velocity distribution of sputtered neutrals incident on the substrate surface will be shown and discussed.

9:40am **TF-ThM5 Effects of Steering and Shadowing in Epitaxial Growth***, **J.G. Amar**,* University of Toledo **INVITED**

While shadowing has been known to play a role in some thin-film deposition processes, until recently it has been assumed that in epitaxial growth the effects of steering and shadowing are negligible. Here we present theoretical and molecular dynamics results describing the effects of steering due to both the short-range and the long-range van der Waals attraction on metal (100) and (111) epitaxial growth. Our results lead to a general picture of the process of deposition near step-edges@footnote 1,@@footnote 2@ which is quite different from the standard downward funneling picture. In particular, we find that short-range attraction plays an important role both after as well as before collision with the step. As a result, it can significantly enhance the uphill current, selected mound angle, and surface roughness for typical energies used in epitaxial growth. For the case of deposition on metal (111) surfaces we also find a significant asymmetry between the interaction at A and B steps which may be explained by differences in the step geometry. We have also calculated the van der Waals constant describing the long-range interaction between a Cu atom and a Cu(100) surface. Our result is large enough to explain recent observations@footnote 3@ of a significant increase in mound angle in Cu/Cu(100) growth for large angles of incidence (@theta@ > 50 °) and also indicates that for smaller angles of incidence the dominant effects are due to the short-range rather than to the long-range interaction. Finally, we discuss the effects of shadowing in oblique incidence epitaxial growth and its implications for the formation and control of nanoscale patterning during growth. @FootnoteText@ @footnote 1@ J. Yu and J.G. Amar, Phys. Rev. Lett. 89, 286103 (2002).@footnote 2@ J. Yu and J.G. Amar, Phys. Rev. B 69, 045426 (2004)@footnote 3@ S. van Dijken et al, Phys. Rev. B 61, 14047 (2000).

10:20am **TF-ThM7 Inhomogeneous Transport of Energetic and Thermalized Neutrals in a Magnetron Sputter System***, **F.J. Jimenez**,* University of Alberta, Canada*; S. Leonard,* Matrikon, Canada*; P. Beatty, S. Dew,* University of Alberta, Canada

Thermalization of energetic neutrals in a typical magnetron sputter deposition system occurs as energetic particles collide with background gas atoms. Most of these energetic neutrals are created at the cathode as a result of positive ions striking the target and causing sputter ejection/reflection. After a few collisions these energetic neutrals are greatly slowed until they reach thermal energies and their transport is believed to be governed by diffusion phenomena. This effect is responsible for reducing the energy of incoming particles to the substrate which in turn affects the characteristics of the film being deposited. It is known that island formation and coalescence stages of film growth strongly depend on temperature, angle of incidence and energy of neutrals. A coupled model that approximates transport of the thermalized particles in a typical magnetron sputter chamber is presented. The thermalized model follows a fluid approach to predict steady state spatial distributions of thermalized particles as a function of space. Transport equations are solved in a three dimensional space with a nonuniform grid and anisotropic transport coefficients. Particle diffusion is coupled with a temperature solver to consider the impact of gas heating. Shadowing effects due to the rather complex geometry of a common magnetron chamber are also taken into consideration in the model. Transport of energetic reflected neutrals and sputtered atoms from the target is simulated with a MonteCarlo approach which includes the gas rarefaction and heating effects. A study of the effect that power has on the steady state temperature of the gas is included. The simulation is performed assuming a typical aluminum deposition in an argon environment at constant voltage and pressure. Steady state temperature profiles and particle distributions in the whole chamber are presented indicating a clear temperature dependence on power as previous works have reported.

10:40am **TF-ThM8 A Target Material Pathways Model for High Power Pulsed Magnetron Sputtering***, **D.J. Christie**,* Advanced Energy Industries, Inc.

The potential of high power pulsed magnetron sputtering (HPPMS) has created growing interest, because it can generate a dense plasma with high target material ion content. However, deposition rates are significantly lower than for DC sputtering at the same average power.@footnote 1@@super ,@@footnote 2@ The HPPMS rates are typically only 25% to 35% of the DC rates at the same average power when the process parameters are equal. The fraction of target material arriving at the workpiece which is ionized ranges from 5% to 70%@footnote 3@@super ,@@footnote 4@@super ,@@footnote 5@ as reported so far by workers in the field. Optical emission spectroscopy suggests a highly metallic plasma, but even so, the fraction of ionized target material arriving at the workpiece can be low. A simple pathways model has been developed to explain these experimental results. In addition, parametric evaluation of the model suggests target material characteristics which are desirable in order to achieve higher deposition rates and a greater ionized fraction of target material reaching the substrate. The model will be presented, with representative characteristic results and implications on HPPMS processes. In addition, insights from approximate model equations and their significance will be presented. @FootnoteText@ @footnote 1@J. A. Davis et al., to be published in Proc. 47th Annual SVC Tech. Conf., (2004).@footnote 2@W. D. Sproul et al., to be published in Proc. 47th Annual SVC Tech. Conf., (2004).@footnote 3@V. Kouznetsov et al., Surface and Coatings Technology 122, 290 (1999).@footnote 4@A. P. Ehiasarian et al., Surface and Coatings Technology 163-164, 267 (2003).@footnote 5@B. M. DeKoven et al., Soc. of Vac. Coaters 46th Annual Tech. Conf. Proc., 158 (2003).

11:00am **TF-ThM9 Complex Target Poisoning Effects in Reactive Sputtering**, ***D. Rosen**, O. Kappertz, T. Nyberg, I. Katardjiev, S. Berg,* Uppsala University, Sweden

Target poisoning is the major factor limiting the deposition rate in reactive sputtering processes. Chemisorption of the reactive gas at the target surface is the main poisoning mechanism which has been studied in detail and is realatively well understood. However, there are both experimental and theoretical indications that there exists an additional target poisoning process taking place simultaneously with chemisorption. This is implantation of ionized reactive gas molecules into the subsurface of the target. These ions will penetrate some 40-80 Angstrom beneath the surface depending on target voltage. At this position these molecules will also undergo chemical reactions with the target metal atoms and form compound molecules. The target is continously etched by the mixture of energetic argon ions and ionized reactive gas molecules. Thus, the compound molecules formed by ion implantation will be brought to the surface as the target is etched. In this way additional compound molecules will be brought to the surface as compared to the case when only chemisorption at the surface would have taken place. We present a simple treatment for how these two target poisoning mechanisms will affect the processing behaviour of the reactive sputtering process. Our results indicate that the chemical reactivity between the target metal atoms and reactive gas molecules will determine if chemisorption or ion implantation is the dominating mechanism for taget poisoning. The most surprising result, however, is that we found that due to recoil implantation with the energetic argon ions the depth of the partly formed compound sub-layer will be almost identical irrespective whether chemisorption or ion implantation is the dominating target poisoning mechanism.

11:20am **TF-ThM10 Process Parameter - Film Structure/Optical Property Study of Reactive Sputter Deposited Hafnium Dioxide**, ***E. Hoppe**, C.R. Aita,* University of Wisconsin-Milwaukee

HfO@sub 2@ is a refractory material that has gained importance in thin films for high k, high n, wide band gap applications. Here, we deposited HfO@sub 2@ films by sputtering a Hf target in rf-excited Ar/O@sub 2@ discharges. 150-nm thick films were grown at room temperature on Si and fused SiO@sub 2@ substrates. Nine combinations of cathode voltage (500 to 1000 V) and O@sub 2@ gas content (10 to 40%) were used. Our goal was to determine the relationship between deposition process parameters and the films atomic structure (long and short range order) and near ultraviolet-visible-infrared absorption and reflection behavior. X-ray diffraction showed the following results: (1) All films were nanocrystalline with monoclinic (m) HfO@sub 2@, the STP phase, predominant. (2) For a fixed cathode voltage, m-HfO@sub 2@ orientation with respect to the substrate was strongly dependent upon the gas O@sub 2@ content. Specifically at high gas O@sub 2@ content, a preferred m(11-1) orientation, the lowest energy growth orientation, was observed. Other orientations of m-HfO@sub 2@ became strong at low gas O@sub 2@ content and low cathode voltage, including a preferred m(111) orientation. (3) A trace amount of tetragonal (t) HfO@sub 2@, a high temperature phase, was observed in some films. This phase was possibly stabilized by a finite crystal size effect, analogous t-ZrO@sub 2@. However, the tetragonal phase occurs in significant amounts in ZrO@sub 2@ but in trace amounts in HfO@sub 2@ films grown under similar conditions, suggesting that the critical radius above which t transforms to m is smaller in HfO@sub 2@ than in ZrO@sub 2@ films, consistent with a lower t-to-m transformation temperature in bulk ZrO@sub 2@. All films are highly transparent. Transmission v. wavelength curves yielded an optical band gap of ~6.4 eV. Optical absorption edge characteristics were independent of film nanocrystal orientation, consistent with this property depending chiefly upon short-range order in wide band gap oxides.

11:40am **TF-ThM11 Integrated Modeling of Al@sub 2@O@sub 3@ Atomic Layer Deposition**, ***H. Simka**, D. Thakurta, S. Shankar,* Intel Corp.

Atomic Layer Deposition (ALD) has become an increasingly attractive option for deposition of various crucial semiconductor material layers, including high-K dielectrics and barrier metal applications. ALD advantages, which include excellent film coverage, uniformity, composition and thickness targeting, can be realized by optimizing precursor reactivity and process conditions. Fundamental understanding of these factors is often limited, especially for surface reaction pathways involving new materials. One possible approach, based on first-principles quantum chemistry investigations of precursor reactions, is described in this work. The goal of this general approach is to reduce the amount of process characterizations needed, and to complement available surface science and growth data. As an example, Density-Functional Theory was used to determine molecular properties and reaction energy barriers for Al@sub 2@O@sub 3@ ALD with Trimethylaluminum (TMA) and H@sub 2@O precursors, building on results from a previous quantum chemical study (1). A reaction mechanism containing important surface reactions controlling ALD behavior was developed, and integrated with a reactor model. The approach was validated against Al@sub 2@O@sub 3@ ALD data in a well-characterized flow-tube reactor (2). Model predicted growth rates in excellent agreement with data, and explained effects of process conditions (temperature, pressure, precursor cycle-times) on ALD growth. Differences in species reactivity on both alumina (important for growth) and silica substrates (important for nucleation) will be discussed. Acknowledgements: Prof. Steven George (U. Colorado-Boulder), Prof. Charles Musgrave (Stanford U.). References: (1) Y. Widjaja and C.B. Musgrave, Applied Physics Letters, 80(18), 3304 (2002) (2) J.W. Elam, M.D. Groner, and S.M. George, Review of Scientific Instruments, 73(8), 2981 (2002).

Technology for Sustainability
Room 303D - Session TS-ThM

Sustainable Manufacturing, Nanotechnology, and Environmental Policy

Moderator: P. Maroulis, Air Products and Chemicals, Inc.

9:00am **TS-ThM3 Engineering, Business, and the Next Environmental Frontier: Will Sustainability Solutions Self-Assemble?**, ***S.J. Skerlos,*** The University of Michigan at Ann Arbor **INVITED**

This presentation highlights the central role of business and engineering in the Next Environmentalism. Characteristics of sustainable design and principles of green engineering are discussed in the context of numerous manufacturing examples in the automotive and consumer electronics industries. Such examples are also utilized to demonstrate incentives and inhibitors to accelerated corporate adoption of sustainability practices.

9:40am **TS-ThM5 Emerging Applications for Electrodeposited Nano-Structured Materials: Environmental Benefits and Potential Risks**, ***G. Palumbo,*** Integran Technologies, Inc., Canada **INVITED**

From the first engineering structural application for nanostructured materials in 1993 (the Electrosleeve process for nuclear component repair), electrodeposition has emerged as one of the most simple and cost-effective ‘bottom-up’ manufacturing methods for the commercial-scale production of a wide variety of nanostructured product forms, including powders, foams and fully-consolidated, net shape nano-structured components. In this presentation, an overview is provided of the electroforming production method, as well as of some of the unique functional and structural properties possessed by these materials. Particular emphasis will be placed on current and near-term applications where this technology can provide significant environmental benefits such as (1) replacement of hard chromium electroplating, (2) elimination of toxic metals in electronic materials, (3) enhanced energy efficiency through the emergence of superior soft magnetic materials, (4) anti-bacterial products, etc. These environmental benefits are discussed in the light of potential risks to human health associated with the possibility of more widespread release of ultra-fine metal/ceramic particulate to the environment.

10:20am **TS-ThM7 Designing More-sustainable Technologies through Green Chemistry and Nanoscience**, ***J.E. Hutchison,*** University of Oregon **INVITED**

Traditionally, materials design and utilization has been guided primarily by product/process performance and economic considerations. However, some of the materials used and manufactured today pose threats to human health, the environment, worker safety, and security. There is an increasing need for products and manufacturing processes that are measurably more sustainable than those currently available. Green chemistry and engineering principles can be adopted to guide the early stages of product and process development to meet this demand. Nanotechnology provides another important opportunity for the development of sustainable technologies. This is because nanotechnology (i) is in the early stages of development and (ii) it offers the promise of new material properties that can be tapped for innovation. In this presentation, I will discuss how green chemistry and engineering principles can guide the responsible development of nanotechnology and how nanoscience can enable the discovery of greener products and processes. Examples of greener materials, processes and applications developed through nanoscience will be presented.

11:00am **TS-ThM9 Nanotechnology and Environmental Policy*, S. Davis,*** Silicon Valley Toxic Coalition **INVITED**

Nanotechnology and Environmental Policy: Nanotechnology refers to the ability to restructure materials at the atomic level. The term nanotech is broadly applied to today’s use of nanoparticles in cosmetics or industrial coating as well as the long term goal of molecular manufacturing, which is the use of self replicating nanoparticles to mass produce almost any type of products. Nanotechnology today bears similarities to the micro electronic industry of the 1970’s. Like the micro electronics industry, nanotechnology is touted as a clean industry and it is expected to solve problems in medicine, manufacturing, computer science and energy storage. Also reminiscent of the micro electronic industry of 30 years ago, the nanotech industry is largely unregulated. New products using nanomaterials are being introduced to the market without adequate environmental health or life-cycle assessment. Silicon Valley Toxics Coalition (SVTC), a northern California nonprofit organization that researches and advocates on environmental issues associated with the high tech industry, is currently exploring environmental and public health issues associated with nanotechnology. SVTC is researching public policies and environment lessons learned from the micro electronic and biotechnology industries, to identify key environmental health regulatory issues for the emerging nanotechnology industry. SVTC proposes to present the preliminary research and findings on nanotechnology and environmental policy issues at the AVS in November. SVTC findings and a final report will be presented in the Winter of 2005 at a workshop hosted by SVTC for environmentalist, scientist, public health officials and lawmakers.

Applied Surface Science
Room 210A - Session AS-ThA

Fuel Cell, Catalytic, and Nanomaterials Characterization

Moderator: B. Beard, Akzo Nobel Chemicals

2:20pm **AS-ThA2 Nanoscale Effects on Ion Conductance of Layer by Layer Structures of Gadolinia-doped Ceria and Zirconia***, **S.A. Azad**, A.A. El-Azab, L.S. Saraf, O.M. Marina, C.W. Wang, D.E. McCready, S.V. Shutthanandan, S.T. Thevuthasan,* 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 yttria-stabilized zirconia, the major component currently used in solid oxide fuel cells (SOFC). In this research, we have synthesized layer by layer structures of gadolinia doped ceria and zirconia in order to determine the nanoscale effects on the ion conductance of these films. Highly oriented multilayered nanostructures of gadolinia-doped ceria and zirconia were grown on sapphire substrates using molecular beam epitaxy and were characterized by in situ reflection high energy electron diffraction (RHEED) and ex situ x-ray diffraction (XRD), high resolution transmission electron microscopy (HRTEM) and Rutherford backscattering spectrometry (RBS). The oxygen ion conductance, measured by surface impedance spectroscopy at relatively low temperatures, was found to increase with increasing number of layers in these films. 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 solid oxide materials. The defect electrochemistry model developed in our study allows the extrinsic element (Gd) to transfer across the interfaces and space charge regions are created as a result, counterbalancing the purely blocking effect observed in polycrystalline structures of ceria or zirconia. The elastic interactions in ceria and zirconia lattice as well as the individual layer thickness largely influence the transfer of Gd across the interfaces.

2:40pm **AS-ThA3 Physical and Chemical Properties of Ce@sub1-x@Zr@subx@O@sub2@ Nanoparticles and Ce@sub1-x@Zr@subx@O@sub2@(111) Surfaces: Synchrotron-based Studies***, **X. Wang**, J.A. Rodriguez, G. Liu, J.C. Hanson, J. Hrbek,* Brookhaven National Laboratory*; C.H.F. Peden,* Pacific Northwest National Laboratory*; A. Iglesias-Juez, M. Fernández-García,* Instituto de Catálisis y Petroleoquímica, CSIC, Spain

The physical and chemical properties of Ce@sub1-x@Zr@subx@O@sub2@ nanoparticles and Ce@sub1-x@Zr@subx@O@sub2@(111) surfaces (x@<=@0.5) were investigated with synchrotron-based techniques (high-resolution photoemission, time-resolved X-ray diffraction and X-ray absorption near-edge spectroscopy). CeO@sub2@ and Ce@sub1-x@Zr@subx@O@sub2@ particles in sizes between 3 and 7 nm were synthesized using a novel microemulsion method. The results of XANES (O K-edge, Ce and Zr LIII-edges) indicate that the Ce@sub1-x@Zr@subx@O@sub2@ nanoparticles and Ce@sub1-x@Zr@subx@O@sub2@(111) surfaces have very similar electronic properties. The lattice constant decreased with increasing Zr content, varying from 5.40Å in CeO@sub2@ to 5.27Å in Ce@sub0.5@Zr@sub0.5@O@sub2@. Within the fluorite structure, the Zr atoms exhibited structural perturbations that led to different types of Zr-O distances and non-equivalent O atoms in the Ce@sub1-x@Zr@subx@O@sub2@ compounds. The nanoparticles were more reactive towards H@sub2@ and SO@sub2@ than the (111) surfaces. The Ce@sub1-x@Zr@subx@O@sub2@(111) surfaces did not reduce in hydrogen at 300°C. At temperatures above 250°C, the Ce@sub1-x@Zr@subx@O@sub2@ nanoparticles reacted with H@sub2@ and water evolved into gas phase. XANES showed the generation of Ce@super3+@ cations without reduction of Zr@super4+@. There was an expansion in the unit cell of the reduced nanoparticles probably as a consequence of a partial Ce@super4+@-->Ce@super3+@ transformation and the sorption of hydrogen into the material. S K-edge XANES spectra pointed to SO@sub4@ as the main product of the adsorption of SO@sub2@ on the Ce@sub1-x@Zr@subx@O@sub2@ nanoparticles and Ce@sub1-x@Zr@subx@O@sub2@(111) surfaces. Full dissociation of SO@sub2@ was seen on the nanoparticles but not on the (111) surfaces. The metal cations at corner and edge sites of the nanoparticles probably play a very important role in interactions with the H@sub2@ and SO@sub2@ molecules.

3:00pm **AS-ThA4 Physical and Chemical Properties of Iron and Iron-Oxide Nanoparticles @footnote 1@***, **D.R. Baer**, J.E. Amonette,* Pacific Northwest National Laboratory*; J. Antony,* University of Idaho*; J.C. Linehan, D.W. Matson,* Pacific Northwest National Laboratory*; J.T. Nurmi,* Oregon Health and Sciences University*; K.H. Pecher,* Pacific Northwest National Laboratory*; R.L. Penn,* University of Minnesota*; Y. Qiang,* University of Idaho*; P.G. Tratnyek,* Oregon Health and Sciences University

Iron particles in solution have interesting and potentially useful chemical properties, including an ability to reduce chlorinated hydrocarbons in geochemical environments. Reaction studies indicate that the dechlorination reaction pathway can be altered by the structure and chemistry of the nanoparticles. To understand some of these effects we are synthesizing, characterizing, and examining the properties of Fe nanoparticles using a variety of methods. We have synthesized particles in solution and by vapor deposition methods and obtained commercially available materials for detailed study. Methods of particle characterization include TEM, XAS, Mossbauer, XRD, and XPS. A variety of properties are being examined including stability, physical, chemical and electronic structure, magnetic properties and reactivity. Similarities and differences of particles formed in different ways will be discussed along with results relating to particle stability and the impact of particle preparation and processing on reactivity in solution. @FootnoteText@ @footnote 1@ This work is supported by the US Department of Energy Office of Science and parts of the work were performed in the Environmental Molecular Sciences Laboratory a national scientific user facility sponsored by the DoE's Office of Biological and Environmental Research.

3:20pm **AS-ThA5 High-Pressure X-Ray Photoelectron Spectroscopy for Catalysis Research and Environmental Science***, **H. Bluhm**, D.F. Ogletree,* Lawrence Berkeley National Lab*; G. Ketteler,* Lawrence Berkeley National Lab, Univ. of California*; M. Haevecker, A. Knop-Gericke, E. Kleimenov, D. Teschner,* Fritz Haber Inst. of the Max Planck Society, Germany*; E.L.D. Hebenstreit,* Lawrence Berkeley National Lab*; V.I. Bukhtiyarov,* Boreskov Inst. of Catalysis, Russia*; M.K. Gilles, T. Tyliszczak,* Lawrence Berkeley National Lab*; R. Schloegl,* Fritz Haber Inst. of the Max Planck Society, Germany*; M. Salmeron, D.K. Shuh,* Lawrence Berkeley National Lab

High-pressure X-ray photoelectron spectroscopy is a versatile method for the study of gas/solid and gas/liquid interfaces. Recently two synchrotron-based high-pressure XPS spectrometers have been developed, one located at the Molecular Environmental Science beamline at the Advanced Light Source in Berkeley, the other operating at BESSY in Berlin. We have used these high pressure XPS instruments to investigate problems in environmental science and heterogeneous catalysis. In this talk we will discuss the influence of the gas phase on the XPS spectra. Since the incident X-ray beam does not only irradiate the sample surface but also the gas phase in front of the sample, gas phase XPS peaks appear alongside the surface peaks at sufficiently high pressures. The gas phase signal can be used to probe the composition of the gas in the volume in front of the sample and get information about, e.g. the conversion and yield in heterogeneous catalytic reactions. An important group of materials in environmental science are minerals, which are often insulators and therefore charge when irradiated by X-rays. However, the sample surface is discharged due to the ionization of the gas phase by the incident X-rays. The amount of this effect depending on gas pressure and composition will be discussed. We will also consider the proper referencing of the binding energy, and the FWHM of the gas phase peaks depending on gas pressure and work function of the surfaces in the vicinity of the probed gas phase volume. @FootnoteText@ The Advanced Light Source and this work are supported by the Director, Office of Science, Office of Basic Energy Sciences, Division of Materials Sciences and the Division of Chemical Sciences, Geosciences, and Biosciences of the U.S. Department of Energy at Lawrence Berkeley National Laboratory under Contract No. DE-AC03-76SF00098.

3:40pm **AS-ThA6 The Structure and Growth of Single- and Double-Walled Carbon Nanotubes***, **J.-M. Zuo**,* University of Illinois at Urbana-Champaign **INVITED**

Single- and double-walled carbon nanotubes have potential applications for future electronics and nanomachines. However, as-grown carbon nanotubes have a dispersion of structures, which differ in both diameter and chirality, and electric and mechanical properties. Characterization of these nanotubes has been a challenge. Recently, we developed a coherent electron diffraction/imaging technique by forming a nanometer-sized parallel beam of electrons that can be used to record diffraction patterns from individual nanotubes. Furthermore, the combination of coherence and high angular resolution allows the over-sampling of diffraction pattern and solution of phase problem by ab initio phase retrieval, thus, imaging of carbon nanotubes. Using this technique, we have investigated a large number of single- and double-walled carbon nanotubes. We found that neither zig-zag nor arm-chair tubes is preferred for growth. Double-walled carbon nanotubes are generally incommensurate and there is a peaked distribution of spacings between two tubes. The implication of these findings will be discussed based on the growth mechanism of carbon nanotubes. The technique of coherent electron nanodiffraction and diffractive imaging by the solution of the phase problem is general and applicable to other nanostructures. @FootnoteText@ *In collaboration with J. Tao, J. Bording, Boquan Li, M. Gao, L. Nagahara, R. Zhang, R. Twesten and I. Petrov.

4:20pm **AS-ThA8 Carbon Nanotubes and Mo@sub 2@C Reduced Pt Usage for Fuel Cells***, **T. Matsumoto**, T. Komatsu,* University of Tsukuba, Japan*; Y. Chiku,* Sekisui Chemical Co., LTD., Japan*; Y. Nagashima, T. Yamazaki, E. Yoo,* University of Tsukuba, Japan*; H. Shimizu, Y. Sato, Y. Takasawa,* Sekisui Chemical Co., LTD., Japan*; J. Nakamura,* University of Tsukuba, Japan

Pt has been considered to be an essential catalyst for the polymer electrolyte fuel cell (PEFC), and one of the difficulties in spreading fuel cells due to the high price, limited resource and no substitute of Pt. We successfully reduce Pt loads by using carbon nanotubes and Mo@sub 2@C. The PEFC with the 0.2 mg/cm@super 2@-Pt/CNT catalyst is fond to show higher cell voltage at 0-600 mA/cm@super 2@ than that of the PEFC with the 0.5 mg/cm@super 2@-Pt/CB catalyst. The PEFC with the only 0.06 mg/cm@super2@-Pt/CNT gives more than 60% of the cell voltage of the PEFC of the 0.5 mg/cm@super 2@-Pt/CB catalyst at 0-600 mA/cm@super 2@. Carbon nanotubes (CNTs) are better electrodes of Pt than carbon blacks (CBs) presumably due to the more triple-phase formation, better conductivity and more space for gas diffusion [J. Nakamura et al., Chem. Comm., 2004, 840 and Catal. Today, in press]. TEM images showed that 2-4 nm Pt nanoparticles are deposited on the CNT surfaces. The Pt nanoparticles from H@sub 2@PtCl@sub 6@ are well-dispersed, while those from K@sub 2@PtCl@sub 4@ are agglomerated due to an auto catalytic reaction. XPS spectra show Pt was fully reduced to be deposited as metallic Pt nanoparticles. The pretreatment of CNTs to remove amorphous carbon is also important, and a careful treatment is necessary for dissolution by HNO@sub 3@ not to form bundles. We also find that Mo@sub 2@C can be a substitute of Pt for PEFC. It is surprising that a PEFC with the Mo@sub 2@C/CNT catalyst in the anode exhibits 60% cell voltages of the current PEFC with the Pt/CB catalyst (0.5 mg/cm@super 2@). XPS and XRD showed that Mo was fully carburized to form Mo@sub 2@C nanoparticles.

4:40pm **AS-ThA9 Surface Characterization and Surface Science Needs in Support of Automotive Fuel Cells***, **F.T. Wagner**,* General Motors Fuel Cell Activities **INVITED**

Polymer electrolyte membrane fuel cells (PEMFC's) show promise as power sources for high-efficiency light-duty vehicles giving very low emissions. This talk reviews some of the critical interfacial phenomena that must be understood if this promise is to be fully realized. Examples will be given of cases where surface analytical techniques have provided useful insights. Additional cases will be discussed in which extension beyond the capabilities of current surface analytical techniques will be required if critical information is to be obtained. Fuel cells predate the internal combustion engine, but two developments since the 1980's led to the ten-fold increase in power density that generated the current enthusiasm for automotive PEMFC's. First, catalyst makers learned to pack ~3x10@super20@ active platinum sites into a cubic cm of porous catalyst layer through the synthesis of ~50% Pt (by weight) catalysts with >25% dispersion on carbon supports with high electronic conductivity. Second, incorporation into the catalyst layer of ionomer similar to that used in the membrane allowed adequate ionic conductivity to be maintained between these active sites and the electrolyte membrane. While the resulting complex nanostructures must maintain some water content to allow ionic conductivity, excessive retention of product water can prevent access of the gaseous reactants to the catalyst particles. The system contains many interfaces: gas/liquid, gas/ionomer, liquid/ionomer, ionomer/metal, metal/carbon, ionomer/carbon (and perhaps gas/metal), all of which must be carefully controlled. Vacuum surface analytical techniques have yielded major clues as to why Pt-alloy catalysts, the enhanced activity of which is necessary if automotive cost targets are to be met, can be stable in the strongly acidic PEMFC environment. Similar analytical successes on water/ionomer/Pt/carbon interfaces are needed to speed progress toward fuel cells that fully meet automotive requirements.

Biomaterial Interfaces
Room 210D - Session BI-ThA

Biosensors and Bio-Diagnostics

Moderator: D. Grainger, Colorado State University

2:00pm **BI-ThA1 Multi-analyte Immunoassays in Packed Microcolumns: Design and Analysis***, **G.P. Lopez**,* University of New Mexico **INVITED**

This talk will present recent developments at the University of New Mexico in the development of microfluidic based biosensor systems and their use in analysis of biomolecular recognition. The method involves real-time detection of soluble molecules binding to receptor-bearing microspheres, sequestered in affinity column-format inside a microfluidic channel. The packed microcolumn format is (1) well suited for enhancing reaction times of analyte with immobilized receptors, (2) compatible with electro-osmotic pumping, and (3) allows detection of multiple analytes. Identification and quantitation of analytes occurs via direct fluorescence measurements or fluorescence resonance energy transfer (FRET). Several immunoassays have been developed that can potentially detect sub-femtomole quantities of antibody with high signal-to-noise ratio and a large dynamic range spanning nearly four orders of magnitude in analyte concentration in microliter to submicroliter volumes of analyte fluid. Kinetic and equilibrium constants for the reaction of this receptor-ligand pair are obtained through modelling of kinetic responses of the affinity microcolumn and are consistent with those obtained by flow cytometry. Because of the correlation between kinetic and equilibrium data obtained for the microcolumns, quantitative analysis can be done prior to the steady state endpoint of the recognition reaction. This method has the promise of combining the utility of affinity chromatography, with the advantage of direct, quantitative, and real-time analysis and the cost-effectiveness of microanalytical devices. The approach has the potential to be generalized for high sensitivity, high selectivity, rapid detection of a host of bioaffinity assay methods and analyte types.

2:40pm **BI-ThA3 Biosensing Based on Light Absorption of Immobilized Metal Nanostructures***, **F. Frederix**, K. Bonroy, G. Reekmans, C. Van Hoof,* IMEC, Belgium*; G. Maes,* K.U.Leuven, Belgium

The "Transmission Plasmon Biosensor" is a novel, cheap and easy to handle biosensing technique. Surface plasmon resonance sensors are widely used for biosensing. These sensors are highly sensitive to the refraction index at the interface between the metal film deposited upon a prism and a sample upon this metal surface. This principle can also be applied to a dielectric planar surface coated with nanostructures. The plasmon absorption peak position and intensity is highly dependent on the size of these particles and on the close proximity of these particles immobilized onto a surface. This research compromises the synthesis of metal nanoparticles with different sizes and morphologies, which were covalently immobilized on transparent substrates, e.g. glass, quartz and polymers using a molecular glue of silane layers. Particle films were also realized using various evaporation strategies, e.g. thermal evaporation, e-beam evaporation, sputtering and electroless plating. The different strategies were evaluated using TEM, AFM and absorption spectroscopy. The resulting plasmon resonance and interband absorption bands in the visible and UV region were compared. Mixed SAMs were used to couple antibodies to the metal nanoparticle films. The change in absorbance properties of the nanoparticle films upon antibody-antigen binding was monitored in order to obtain quantitative information on the antibody-antigen interaction. Besides the localised plasmon resonance sensing, we observed a novel physical phenomenon namely the interband 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 the implementation into an array technology. The Transmission Plasmon Biosensor fulfils therefore the needs of an ideal, multi-analyte bio(nano)sensor.

3:00pm **BI-ThA4 2-D Array Biosensor using Waveguide Bragg Grating***, **K.S. Choi**, H.J. Lee, C.I. Jung, H.J. Park, N.W. Park,* Chonnam National University, Korea

Bragg grating based planar integrated optical circuit technology is applied to biosensors. Varieties of detection mechanisms such as antigen-antibody are investigated and an appropriate structures of Bragg grating optical sensors circuit is demonstrated. Trenches are fabricated onto a planar waveguide substrate and polymer core material with high refractive index is deposited in these trenches.Bragg gratings are formed onto this polymer core and series of Bragg gratings with different periods are fabricated along these waveguides. These waveguides are repeated in serial such repetition makes 2-D array of bio sensors which might be vey effective in sensing of disease. We will introduce and demonstrate the Bragg grating based silica waveguide sensors in this paper and some theoretical designs will be considered.

3:20pm **BI-ThA5 Biological Sensors Based on Brownian Relaxation of Magnetic Nanoparticles***, S.-H. Chung, A. Hoffmann,* ***S.D. Bader****, L. Chen, C. Liu, B. Kay, L. Makowski,* Argonne National Laboratory

We present a biological sensing platform that is based on a modification of the dynamic magnetic properties of ferromagnetic nanoparticles suspended in a liquid. For a narrow size range the ac magnetic susceptibility of the ferromagnetic nanoparticles is dominated by Brownian relaxation. By coating the nanoparticles with a suitable ligand the Brownian relaxation and thus the ac magnetic susceptibility can be modified through the binding to the corresponding bio-receptor. The size of the particles has to be large enough to avoid superparamagnetism and at the same time small enough to have a homogeneous single domain magnetization. We demonstrate a proof-of-principle of this concept by using avidin-coated Fe@sub 3@O@sub 4@ particles that are ~10 nm in diameter, which were investigated before and after binding to biotinylated S-protein and bacteriophage particles. The ac susceptibility measurements show that the magnetic relaxation occurs via a Brownian mechanism; the frequency shift for the peak in the imaginary part of the susceptibility after binding to the target indicates the increase of the hydrodynamic radius. We are currently developing magnetic phage viruses in order to further improve this bio-sensing platform. @FootnoteText@ * Supported by DOE, BES under contract W-31-109-ENG-38, and DARPA under contract 8C67400.

3:40pm **BI-ThA6 G-Protein Coupled Receptor Biosensors - New Opportunities and Applications***,* ***E.J. McMurchie****, W.R. Leifert,* CSIRO Health Sciences and Nutrition, Australia*; L. Wieczorek, B. Raguse,* CSIRO Telecommunications and Industrial Physics, Australia **INVITED**

Future diagnostic and biosensor platforms will require development of cell-free, high-throughput, microarray formats with bioengineered sensors mimicking the specific interactions between ligand and cell membrane receptors. For bio-diagnostic technologies, G-protein coupled receptors (GPCRs) are likely to have application as biosensors reporting on ligands influencing physiological and pathophysiological functions. GPCRs are a large and ubiquitous class of membrane-associated receptors activated by a wide range of extracellular ligands, (biogenic amines, amino acids, ions, peptides, and bioactive lipids) which act as hormones, neurotransmitters, chemokines etc. Signalling through these receptors regulates responses such as neurotransmission, chemotaxis, inflammation, cell proliferation, muscle contractility, and visual and chemosensory perception. GPCRs signal to numerous down stream cellular effectors via a set of heterotrimeric G-proteins through GTP dependant processes. GPCRs are the target for >50% of current therapeutic drugs with drug discovery programs relying on high throughput screening technologies. The future development of microarray technologies for GPCRs is relevant for the development of highly specific ligands in drug discovery and for utilising GPCRs as potential biosensors. Present assays for ligand screening against GPCRs can be classified into two major categories; whole cell assays with cell-associated, down-stream signalling systems for detecting activated receptors, and homogeneous, cell-free assays consisting of membrane fragments containing (usually cloned) GPCRs. For the latter, some form of signalling/reporting system must be added if functional assays, as opposed to ligand binding, are to be used. Our strategic objective is the construction of a cell-free system to enable reconstitution and nanoconstruction onto appropriate surfaces for future adaptation to microarray formats suitable for high throughput, multiplex screening.

4:20pm **BI-ThA8 Detection of Human Immunodeficiency Virus-1 Using Micro-Cantilever Deflection Biosensors***, Y. Lam,* ***N. Abu-Lail****, M. Alam, S. Zauscher,* Duke University

Having a simple, efficient, and sensitive technique for the diagnosis of human immunodeficiency virus-1 (HIV-1) is extremely important due to the increasing trend in HIV-1 cases, and the current lack of a rapid and simple method to detect the disease. We show that surface modified micro-cantilevers, decorated with monoclonal antibodies (mAb) A32, deflect upon specific binding of mAb A32 to HIV-1 envelope glycoprotein gp120 (HIV-1 Env gp120). This deflection of the micro-cantilever is a direct result of the surface stress induced by molecular recognition mediated protein binding. The specific binding between the two proteins was confirmed through force spectroscopy measurements between mAb 17b tethered to a surface and HIV-1 Env gp120 immobilized on the cantilever; HIV-1 gp120 will only bind mAb 17b if the former has bound to mAb A32. Our results show that micro-cantilever deflection can effectively be used for the sensitive detection of molecular recognition events, encouraging the further development of this technique as a rapid response biosensor for disease diagnosis. Work on determining the detection limits of the micro-cantilever deflection method and its extension to whole virus detection is in progress.

4:40pm **BI-ThA9 Realization and Characterization of Porous Gold for Increased Protein Coverage for Biosensor Applications***,* ***K. Bonroy****, J.-M. Friedt, F. Frederix, R. De Palma,* IMEC, Belgium*; M. Sàra,* Center for NanoBiotechnology, Austria*; B. Goddeeris,* KULeuven, Belgium*; G. Borghs,* IMEC, Belgium*; P. Declerck,* KULeuven, Belgium

In recent years, there has been an increasing need for the detection of biochemical substances with low molecular weight. Biosensors could be an alternative to conventional analytical methods for monitoring these substances. However, generally applied biosensor systems are often not sensitive enough for direct detection of these compounds. Therefore, our research focuses on the development of biosensors with improved transducer capabilities and biological interfaces. We chose gold surfaces in combination with SAMs of thiols as platform for the immobilization of biomolecules because of its compatibility with existing biosensors. In previous research, the use of SAMs of thiols on flat gold surfaces showed several advantages concerning specificity and reproducibility for final biosensor applications. However, the main disadvantage of this approach is the 2D aspect of these layers compared to 3D surfaces (e.g. polymers). 3D surfaces, such as porous gold, would allow for the immobilization of a large number of molecules per surface area, facilitating higher biosensor responses. The presented research describes the analysis of the different parameters, which define the electrochemical growth of porous gold, starting from flat gold. QCM-D technique was used for online monitoring of the porous gold deposition. The resulting surfaces were characterized using SEM, cyclic voltammetry and contact angle measurements. Applied potentials of -0.5V were found to be the most adequate conditions to grow porous gold, resulting in a 16x increase in surface area. In addition, we evaluated the immobilization degree of S-layer and IgG proteins on these porous surfaces. The optimized deposition conditions for realizing porous gold substrates, lead to 3x increase of S-layer adsorption and 5x increase of anti-IgG recognition using QCM-D as biological transducer. We can conclude that the high specific area of the porous gold amplifies the final sensitivity of the original flat surface device.

Dielectrics
Room 304B - Session DI+PS-ThA
Oxides on Semiconductors

Moderator: S.A. Chambers, Pacific Northwest National Laboratory

3:40pm **DI+PS-ThA6 Crystalline Oxides on Semiconductors, from Interface Structure to Electrical Properties***,* ***F.J. Walker****,* University of Tennessee*; C.A. Billman,* Penn State University*; M. Buongiorno-Nardelli,* North Carolina State University*; R.A. McKee,* Oak Ridge National Laboratory **INVITED**

From the point of view of synthesis using molecular beam epitaxy (MBE) and understanding using tools developed from first principle theory like density functional theory (DFT), a metal oxide semiconductor (MOS) device can be described as an epitaxial superlattice where each atomic layer is well-defined. This view is becoming increasingly germane to device physics as dimensions are scaled down to the atomic level. In this paper we discuss the fundamental interplay of the physical structure, as determined by reflection high energy electron diffraction (RHEED), and the electrical properties, as determined by frequency-dependent electrical impedance measurements and x-ray photoelectron spectroscopy (XPS), for the crystalline oxide on semiconductor system. We show that an interface phase is particularly important to structure and electrical properties for alkaline earth oxides grown on silicon and germanium. The interface phase begins as a surface phase of strontium silicide and transforms to an interface phase through a structural transition. The final structure and composition of the interface phase determines the band offset, interface state density and serves as a template for the epitaxial growth of the alkaline earth oxides. Office of Basic Energy Sciences, U.S. Department of Energy at Oak Ridge National Laboratory under contract DE-AC05-00OR22725 with UT-Battelle, LLC and at the University of Tennesssee under contract DE-FG02-01ER45937.

4:20pm **DI+PS-ThA8 Ultra Thin Oxides and Nitrides on Si: Growth and Properties***, **P. Morgen**, U. Robenhagen, A. Bahari,* SDU Odense, Denmark*; M.G. Rao,* IISc, India*; K. Pedersen,* Aalborg University, Denmark

Various conditions for slow growth of ultra thin silicon oxides on Si have been studied, at relatively low temperatures and pressures, in an ultra high vacuum environment. In this way a hitherto unknown regime in pressure-temperature space has been discovered including a fast (ballistic) stage terminating with a self-limiting oxidation. This precedes and deviates radically from the high temperature-high pressure Deal-Grove mechanism. Several different schemes are invented leading to oxide thicknesses from about 0.4 to 0.7 nm, with high quality of the interface and uniformity of coverage. Our present and previous studies connect the initial steps of oxygen adsorption and reaction at room temperature with the first steps (and barriers) to form three dimensional oxides on two Si surfaces (111) and (100). The structural information is obtained by following these oxidation reactions with photoemission spectroscopy, including high resolution, surface sensitive core-level photoemission; STM; LEED; optical second harmonic generation spectroscopy, and Auger electron spectroscopy. Similar procedures are followed to create ultra thin nitrides using microwave dissociated nitrogen. This process is already known to be self limiting, but at a somewhat higher film thickness than for the growth of oxides. The prospect of doping these oxides with nitrogen, and these nitrides with oxygen, is also successfully explored.

4:40pm **DI+PS-ThA9 Preparation and Properties of Clean Si@sub 3@N@sub 4@ Surfaces***, **V.M. Bermudez**, F.K. Perkins,* Naval Research Laboratory

Si@sub 3@N@sub 4@ is an important material for use in electronic devices. Thin films of Si@sub 3@N@sub 4@ are used as passivation layers and diffusion barriers in IC's and as protective coatings in disk drives. However, the basic surface science of Si@sub 3@N@sub 4@ films has been impeded by the difficulty in obtaining a clean and undamaged surface. In this work, in-situ chemical methods for preparing atomically clean surfaces of Si@sub 3@N@sub 4@ thin films in UHV have been studied using XPS, UPS, ELS and AES. Prior to UHV studies, the thin films (grown ex situ on Si(100) by LPCVD) were characterized by IR reflection-absorption spectroscopy which showed them to be stoichiometric with a low H content. A two-step process consisting of annealing in a flux of NH@sub 3@ vapor to remove C and vapor deposition of Si (followed by thermal desorption) to remove O is found to be an effective cleaning procedure. Other potential cleaning methods, such as annealing in UHV without in- situ chemical treatment or annealing in a flux of H atoms, were considered and found to be only partly effective. The clean surfaces are disordered, as seen in LEED, but show no evidence of Si-Si bonding (which would indicate N vacancies) in the Si LVV AES or in surface-sensitive Si 2p XPS. Evidence for surface- related features is seen in the N 1s XPS and in ELS data in the region of valence excitations; however, no indication of occupied surface states near the valence band maximum is seen in UPS. Preliminary results for O@sub 2@ chemisorption show adsorbate- induced features in the band gap and also evidence for a reduction in the negative surface potential due to electron traps present on the clean surface.

5:00pm **DI+PS-ThA10 STM, STS, and DFT Studies of SiO Deposition on the Ge(100) Surface***, **T.J. Grassman**, J.Z. Sexton, 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. High defect densities reduce the capacitance of the MOS structure and prevent the modulation of the semiconductor valence and conduction bands via the application of a gate bias. Germanium's intrinsic oxide has been shown to be inadequate for the task of providing a clean interface, therefore an alternative material must be used which can be deposited and grown on the Ge surface. To this end, we are investigating the bonding and electronic structure of the interface between SiO and the Ge(100)-p(2x1) surface using scanning tunneling microscopy (STM), scanning tunneling spectroscopy (STS), and density functional theory (DFT) computational modeling. SiO can act as a precursor to SiO@sub 2@ or as a buffer layer for high-k dielectric growth. We will present atomically resolved images of both the clean Ge(100) and SiO-deposited surfaces at various coverages, along with DFT modeling results of the observed bonding structures. We find that SiO always bonds Si-end down, mostly inserting in between the Ge dimer rows and sometimes into the Ge dimers themselves. Even at modest coverages (> 5%) SiO bilayers are formed via pyramidal (SiO)@sub 3@ molecular structures with Si-O-Si-O bonding configuration. DFT-based STM simulations will be presented to aid in the interpretation of experimental STM images. We will also present STS dI/dV spectra of the associated surface electronic structure (density of states) which show that the SiO/Ge interface yields an unpinned Fermi level.

Electronic Materials and Processing
Room 304B - Session EM-ThA

Multifunctional Materials

Moderator: V.M. Bermudez, Naval Research Laboratory

2:00pm **EM-ThA1 Computational Design of Multifunctional Electronic Materials***, **N.A. Spaldin**,* University of California, Santa Barbara **INVITED**

In this talk we show how modern theoretical and computational methods can be used to design technologically relevant electronic materials with dual- or multi-functionality. We choose multiferroic magnetoelectrics as an example; These are materials that are both ferromagnetic and ferroelectric in the same phase, and therefore have a spontaneous magnetization which can be switched by an applied magnetic field, a spontaneous polarization which can be switched by an applied electric field, and often some coupling between the two. Very few exist in nature, or have been synthesized in the laboratory, so we begin by determining the fundamental physics behind the scarcity of ferromagnetic ferroelectric coexistence. Then we identify the chemistry behind the additional electronic or structural driving forces that must be present for ferromagnetism and ferroelectricity to occur simultaneously. Finally we describe the successful prediction and subsequent synthesis of a new multiferroic material.

2:40pm **EM-ThA3 Tailoring of the Microwave Dielectric Properties of Ba@sub 1-x.@Sr@sub x@TiO@sub 3@ Based Thin Films by Acceptor Doping***, **M.W. Cole**,* U.S. Army Research Laboratory*; R.G. Geyer,* National Institute of Standards and Technology*; W.D. Nothwang,* U.S. Army Research Laboratory

In this work, material compositional design and optimized film processing methods, were employed to simultaneously lower the dielectric loss and enhance the dielectric tunability of Ba@sub 1-x.@Sr@sub x@TiO@sub 3@ (BST) based thin films without compromising the device impedance matching (permittivity less than 500) and device control voltage (less than 10 Volts) requirements. The films compositional design was achieved by Mg doping BST from 3 to 10 mol-percent via the metalorganic solution deposition (MOSD) technique and post-deposition annealing in an oxygen ambience. The films dielectric loss at these doping levels was identical, tan delta of 0.007, and the permittivity values ranged from 339 to 220. Device quality values of tunability, 40 and 32 percent, for the 3 and 7 mol-percent doped BST films, respectively, were achieved by elevating the applied bias to 474 kV/cm. This device quality tuning is compatible with voltage requirements of current semiconductor based systems. The results suggest that the low level acceptor doping from 3 to 7 mol-percent, optimized precursor solution concentration (0.43 M), and oxygenated post-deposition thermal processing were found to work in concert to lower dielectric loss, limit defect density concentration, optimize film microstructure, and eliminate undesirable film/electrode interfacial phases. The enhanced dielectric and insulating properties of the 3 to 7 mol-percent Mg doped BST thin films make them excellent candidates for integration into tunable devices.

3:00pm **EM-ThA4 Strain-effected Phase Transition Temperature of BST Thin Films***, **J.A. Bellotti**, W. Chang, S.B. Qadri, S.W. Kirchoefer, J.M. Pond,* Naval Research Laboratory

Ba@sub 0.5@Sr@sub 0.5@TiO@sub 3@ (BST) thin films were grown on (100) MgO and (100) LaAlO@sub 3@ substrates by rf/magnetron sputtering in the thickness range of 50 to 300 nm. Recent studies have demonstrated the importance of film strain on the microwave frequency electronic properties of ferroelectric thin films. We have observed that stress can result in Curie temperature shifts of nearly 300 K in epitaxial thin films of SrTiO@sub 3@@footnote 1@. These highly strained films are also shown to have large directional dependences on the applied electric field. We report on efforts to relate lattice spacing and the resultant substrate-induced stress, as measured by x-ray diffraction, with the measured Curie temperature and microwave tunability and loss. XRD phase analysis as a function temperature will be correlated with the observed directionally-dependent and temperature-dependent microwave properties. Additional characterization of non-epitaxial films and bulk substrate crystals will be presented as a baseline for understanding the strain effect in thin ferroelectric layers. @FootnoteText@ @footnote 1@"Using Strain to Control Microwave Tunability and Loss in Barium Strontium Titanate Thin Films", AVS 50th International Symposium, Session EM-WeM5, Invited Talk, 2003. .

3:20pm **EM-ThA5 Remote Plasma Enhanced Chemical Vapor Deposition of La2O3**, ***P.R. McCurdy***, *T. Vazquez, S. Kohli, E.R. Fisher,* Colorado State University

Rare earth oxides, such as La@sub 2@O@sub 3@, show potential for high-k gate insulator applications. La@sub 2@O@sub 3@ has a large conduction band offset with Si(100) of 2.3 eV@footnote 1@ and a dielectric constant of ~30 eV.@footnote 2@ La@sub 2@O@sub 3@ films on Si(100) were deposited by remote plasma enhanced chemical vapor deposition (RPECVD), using lanthanum acetyl-acetonate (La(acac)), argon and oxygen. Post deposition annealing was performed to reduce carbon and hydrogen content. Film composition and characteristics were examined using x-ray photoelectron spectroscopy, spectroscopic ellipsometry and XRD. Various parameters have been studied, including gas flow rate, substrate temperature (T@sub s@), temperature of the La(acac), and plasma power. Under optimal conditions we were able to produce La@sub 2@O@sub 3@ films with less than 5% carbon content. This is the first report of La@sub 2@O@sub 3@ being deposited by RPECVD. @FootnoteText@ @footnote 1@ J. Robertson, J. Non-Cryst. Solids 303 (1) (2002) 94.@footnote 2@ A. I. Kingon, J.-P. Maria, S. K. Streiffer, Nature 406(2000) 1032. .

Magnetic Interfaces and Nanostructures
Room 304A - Session MI-ThA

Molecular Spintronics and Dynamics

Moderator: S.E. Russek, NIST

2:00pm **MI-ThA1 Semiconductive Behavior of the Single Molecule Magnets Mn@super12@-Ac, Fe@super8@Br@super8@, and V@super15@**, ***N.S. Dalal***, *E.S. Choi, D. Zipse, R. Vasic, J.M. North, E. Jobiliong, J.S. Brooks,* Florida State University*; P. Kogerler,* Iowa State University **INVITED**

Single Molecule Magnets (SMMs) are clusters of transition metals that have garnered much theoretical and experimental attention due to their ability to show magnetic hysteresis on the single molecule level, and Macroscopic Quantum Tunneling. In order to advance our understanding of these materials for potential applications, the electrical transport properties of three of the most widely studied SMMs, Mn@sub12@-Ac, Fe@sub8@Br@sub8@, and V@sub15@, as well as the polyoxovanadate cluster V@sub12@ were examined. These materials all showed semiconductive behavior, with varying transport gaps, E@suba@, for each. Under the assumption that the optical band gap is twice the magnitude of the transport gap, E@subg@ = 2 E@suba@, the magnitude of the transport gap for Mn@sub12@-Ac (0.37 eV), V@sub15@ (0.2 eV), and V@sub12@ (0.48 eV) compares well with optical band gap measurements@footnote 1@,@footnote 2@ thus verifying the value of transport measurements in electronic structure calculations for SMMs. These data should provide a sensitive basis for comparing the various theoretical calculations and, thus, for understanding the electronic structure of these materials. @FootnoteText@ @footnote 1@ S.M. Oppenheimer, A.B. Sushkov, J.L. Musfeldt, R.M. Achey, and N.S. Dalal, Phys. Rev. B 65, 054419 (2002).@footnote 2@ J.Choi, L.A.W. Sanderson, J.L. Musfeldt, A. Ellern, and P. Kogerler, Phys. Rev. B 68, 064412 (2003). .

2:40pm **MI-ThA3 High Frequency Investigations of Molecular Nanomagnets by use of a Broadband SQUID-Detected Electron Paramagnetic Resonance Probe**, ***B. Cage***, *S.E. Russek,* National Institute of Standards and Technology*; D. Zipse, J.M. North, N.S. Dalal,* Florida State University **INVITED**

We are synthesizing and characterizing (by use of high frequency electron paramagnetic resonance (HFEPR)) molecular nanomagnets (magnetic molecules < 2 nm that behave as single molecule magnetic domains) for high-frequency spintronics applications. We will discuss current efforts to examine the magnetic susceptibility of these nanomagnets as 2-dimensional films vs the 3-dimensional bulk behavior of aligned single crystals. HFEPR data at 95 and 141 GHz, with magnetic resonance fields ranging from 0 - 12 Tesla indicate potential as tunable high-frequency low-applied-field oscillators from 5 - 80 K. This work represents some of the highest temperatures at which these magnets have been characterized, which is of importance for practical spintronics applications. To complement this work we have developed a new experimental technique that uses SQUID detection of the magnetic susceptibility as a function of applied magnetic field through the EPR transition at resonance frequencies > 60 GHz and magnetic fields up to 5 Tesla. One advantage over conventional EPR being the quantitative determination of the level of saturation. We will present data on the large electronic spin (S) S=10 molecular nanomagnet Fe8 that discretely identifies the spin-lattice-relaxation time, T1, of the individual ms quantum spin states. This is in contrast to the current non-resonant techniques, such as AC susceptibility, that only provide information on the global T1 properties averaged across all states.

3:20pm **MI-ThA5 Spin-Dependent Tunneling through Molecules**, ***A.N. Pasupathy,*** Cornell University **INVITED**

We discuss two experiments involving spin-polarized tunneling through molecules. In the first experiment, we study nickel tunnel junctions made using a self-assembled-monolayer of octanethiol as a molecular barrier. The devices exhibit significant magnetoresistance, demonstrating that low-energy electrons can traverse the molecular barrier while maintaining spin coherence. In the second experiment, we measure Kondo-assisted tunneling via a carbon-60 molecule in contact with ferromagnetic nickel electrodes. We find that the Kondo peak in the differential conductance is split, by an amount that decreases as the magnetic moments in the two electrodes are turned from parallel to antiparallel alignment. We observe large negative values of the junction magnetoresistance due to the presence of the Kondo effect. @Footnotetext@In collaboration with J. R. Petta, S. R. Slater, R. C. Bialczak, J. Martinek, J. E. Grose, L. A. K. Donev, P. L. McEuen, D. C. Ralph

4:00pm **MI-ThA7 Excitation of Microscopic Spin Waves in Ultrathin Films by Spin-Polarized Electron Energy Loss Spectroscopy**, *R. Vollmer, W. Tang,* ***M. Etzkorn***, *P.S.A. Kumar,* Max Planck Institute of Microstructure Physics, Germany*; H. Ibach,* Institute for Surfaces and Interfaces, Germany*; J. Kirschner,* Max Planck Institute of Microstructure Physics, Germany **INVITED**

The properties of long wavelength spin waves have been investigated since decades by ferromagnetic resonance (FMR), Brillouin light scattering (BLS) and more recently by time domain optical techniques. The properties of these spin waves are determined largely by macroscopic and static quantities like the magnetization and anisotropy energies. In bulk materials inelastic magnetic neutron scattering can be used to measure microscopic spin waves with wavelength of atomic dimensions. We have shown recently that spin polarized electron energy loss spectroscopy (SPEELS) can be used to study these microscopic spin waves in ultrathin films up to the surface Brillouin zone boundary@footnote 1@. Up to now we have investigated ultrathin films of fcc Co, hcp Co, fcc Fe, fcc Fe, and bcc Fe on various substrates. In most cases the spin wave excitation can be observed as well pronounced peak in the loss spectrum. In this case, the acoustic spin wave branch of the surface spin wave mode can be described surprisingly well by a simple nearest-neighbor Heisenberg model. Nevertheless, the spectra indicate the itinerant character of the spin waves as discussed in Ref.@footnote 2@. The acoustic branch is significantly broadened and no clear indication of an optical mode (expected from a Heisenberg model) could be observed up to now. The spin wave peaks are visible in the SPEEL spectrum only for low (<10 eV) energies of the incident electrons. @FootnoteText@ @footnote 1@ R. Vollmer, M. Etzkorn, P.S. Anil Kumar, H. Ibach, and J. Kirschner, Phys. Rev. Lett. 91, 147201 (2003).@footnote 2@ A. T. Costa, Jr., R. B. Muniz, D. L. Mills, Phys. Rev. B 69, 064413 (2004).

4:40pm **MI-ThA9 Ferromagnetic Resonance: An Ultimate Tool to Study the Dynamical Response of Nanostructured Magnetic Systems**, ***J. Lindner***, Universität Duisburg-Essen, Germany*; K. Baberschke,* Freie Universität Berlin, Germany*; M. Farle,* Universität Duisburg-Essen, Germany **INVITED**

Ferromagnetic resonance (FMR) measurements probe the dynamical response of magnetic systems subsequent to an excitation within the microwave regime. Due to the high sensitivity of FMR this technique is well suited for the investigation of nanostructures and ultrathin magnetic films or multilayers@footnote 1@. As the resonance condition is determined by internal fields in the sample like anisotropy fields or interlayer coupling fields within layered structures, FMR experiments give a direct access to these quantities based on an analysis that uses the Landau-Lifshitz equation of motion. This will be demonstrated for the case of Ni/Cu/Ni and Ni/Cu/Co films grown epitaxially on Cu(100) subtrates. A unique possibility to grow and measure the films within an ultrahigh vacuum environment allows to stepwise study the layered structures and, thus, also to investigate the effect of capping layers. Besides investigating the FMR resonance field a careful analysis of the FMR linewidth yields information about relaxation processes within the magnetic system. From frequency dependent experiments we show for the case of Fe/V multilayers that a purely Gilbert-like damping term is not sufficient to explain the observed values of the linewidth@footnote 2@. In this system the relaxation is strongly influenced by the decay of the uniform precession mode due to two-magnon processes. Finally, also within laterally structured systems FMR can be applied to study magnetic properties. This is demonstrated for the case of monodisperse Co/CoO core/shell particles of about 10nm diameter, for which the temperature dependence of the anisotropy energy is discussed. @FootnoteText@ @footnote 1@ J. Lindner, K. Baberschke, J. Phys.: Condens. Matter 15, R193 (2003); S465 (2003).@footnote 2@ J. Lindner, K. Lenz, E. Kosubek, K. Baberschke, D. Spoddig, R. Meckenstock, J. Pelzl, Z. Frait, D. L. Mills, Phys. Rev. 68, 060102(R) (2003).

Nanometer-scale Science and Technology
Room 213C - Session NS1-ThA

Nanoscale Imaging

Moderator: D.M. Tennant, Lucent Technologies, Bell Laboratories

2:00pm **NS1-ThA1 Single Electron Charging in Individual InAs Quantum Dot Observed by Nonconctact Atomic Force Microscopy**, ***Y. Miyahara**, R. Stomp, S. Schaer, Q. Sun, H. Guo,* McGill University, Canada*; S. Studenikin, P. Poole, A. Sachrajda,* National Research Council, Canada*; P. Grutter,* McGill University, Canada

Understanding the electronic structure of quantum dots (QD) is not only important for application but also of great interest in fundamental physics. Although there have been a number of studies of electronic properties using mainly optical or capacitance spectroscopy techniques, investigating a single QD remains challenging because of the extremely small dot dimensions. Spectroscopic techniques based on scanning probe microscopy have been employed, in particular scanning tunneling spectroscopy (STS). In STS the acquired tunneling spectra feature the Coulomb staircase or/and the discrete energy states of the QD depending on the size of the QD and the tunneling barrier thickness. However, these measurements are limited to substrates with adequate conductivity since a measurable tunneling current of typically 1 pA or more is usually required. Here, we report the first successful observation of the Coulomb blockade effect by electrostatic force measurements. The main experimental features in the electrostatic force vs. the tip-substrate bias voltage curves agree well with a simple theory based on the semi-classical theory of the Coulomb blockade effect. Comparison of the experimental results with the model calculation will be made and the possibility to observe the discrete energy states will also be discussed. One of the important differences to STS is that there is no continuous current flowing in the system. As a consequence, this technique can detect single electron events. Furthermore, this implies that this technique can also be applied to the QDs embedded in other materials.

2:20pm **NS1-ThA2 Nanoelectromechanics of Scanning Probe Microscopies of Ferroelectric Surfaces**, ***S.V. Kalinin,*** Oak Ridge National Laboratory*; A. Gruverman,* North Carolina State University*; J. Shin, A.P. Baddorf,* Oak Ridge National Laboratory*; E. Karapetian, M. Kachanov,* Tufts University

Nanoscale applications of ferroelectric materials including MEMS and nonvolatile memory components have motivated a number of studies of ferroelectric behavior on the nanoscale using a wide array of electromechanical Scanning Probe Microscopy techniques including Piezoresponse Force Microscopy, Atomic Force Acoustic Microscopy, Scanning Near-Field Acoustic Microscopy, and Heterodyne Ultrasonic-Electrostatic Force Microscopy. Quantitative interpretation of SPM domain imaging mechanisms and particularly hysteresis loop measurements and tip-induced polarization switching processes requires description of contact mechanics for the ferroelectric surface including electromechanical coupling effects and also the structure of electroelastic fields inside the material. Here, the analytical solution of the coupled electromechanical problem for piezoelectric indentation is used to derive the relationship between indentation force, tip bias and tip displacement. These stiffness relations are utilized for quantitative interpretation of the imaging mechanism of the electromechanical SPM techniques. The structure of the electroelastic fields yields a quantitative measure of the signal generation volume and also provides a quantitative basis for the analysis of tip-induced polarization switching and local hysteresis loop measurements. The early stages of the switching process require the exact structure of the electroelastic fields to be known, while the late stages of switching processes can be adequately described using point charge type models. Tip-induced switching is shown to be possible only above a minimum threshold tip bias, producing a well-defined minimal size of the switched domain. Approaches to reduce minimal written domain size for ferroelectric lithography and data storage are discussed.

2:40pm **NS1-ThA3 High-Resolution Force Microscopy: Observing Atoms at Work**, ***R. Bennewitz,*** McGill University, Canada*; L. Nony, E. Gnecco, O. Pfeiffer, A. Socoliuc, S. Maier, A. Wetzel, C. Gerber, E. Meyer, A. Baratoff,* University of Basel, Switzerland **INVITED**

Force microscopy has made progress towards quantitative determination of forces with lateral resolution on atomic scale. One example is the observation of enhanceded interactions at the edge atoms of nanoscale pits in KBr surfaces which are able to trap otherwise mobile molecules. Dynamic modes of force microscopy allow to detect dissipative processes with the same lateral resolution. For the molecules trapped in nanoscale pits, a strongly enhanced dissipation is observed compared to the KBr substrate. Dissipation is also the focus of friction force experiments, which recently have revealed new aspects of atomic friction processes, like a regime of ultra-low friction obtained at low loads. New instrumental developments including the combination of a force microscope with mass spectrometer will be discussed.

3:20pm **NS1-ThA5 Imaging of Radiation Effects on an Active Silicon-On-Insulator (SOI) Device using Scanning Capacitance Microscopy (SCM)**, ***C.Y. Nakakura**, M.R. Shaneyfelt, R.A. Jones,* Sandia National Laboratories

Two-dimensional (2D) imaging of electrical properties using atomic force microscopy (AFM)-based techniques has attracted considerable attention in the semiconductor industry, primarily for 2D-dopant profiling of cross-sectioned device junctions. Scanning capacitance microscopy (SCM) has been most widely used for this purpose by acquiring nanometer-scale, 2D free carrier images, from which dopant information can be extracted. The bulk of reported dopant profiling studies using SCM, however, have been performed on shorted, inoperable devices that only show the static device as fabricated. In this study, we expand on conventional, cross-sectional carrier profiling: first, the images were acquired using a modified SCM to permit carrier profiling of active devices and, second, the devices were measured before and after radiation exposure to visualize the effects on device operation. Understanding radiation effects in semiconductor devices is critical to the development of radiation-hardened integrated circuits used in harsh environments, such as Earth-orbit and outer space. We will demonstrate that SCM is a promising tool for directly imaging the effects of radiation in cross-sectioned, silicon-on-insulator (SOI) metal-oxide-semiconductor field-effect transistors (MOSFETs). Following exposure to radiation, the impact of the radiation-induced charge buildup at the Si/SiO@sub 2@ interface of the SOI substrate is readily observed in the SCM images. The methodology of the active device measurements, as well as the implications of radiation exposure on the operation of these devices, will be discussed. @FootnoteText@ 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 **NS1-ThA6 High Resolution Structural and Chemical Information: A Combined STM, SEM and SAM Analysis of Ag Nanocrystallites on Si**, ***J. Westermann**, M. Maier, J. Poppensieker, G. Schaefer,* OMICRON NanoTechnology GmbH, Germany

For the analysis of nanostructured materials it is of crucial importance to be able to characterise not only structural properties of the material, but also determine chemical composition, as well as electronic and magnetic properties of individual nanostructures. To accomplish this, we have combined a high resolution SEM column with an STM under true UHV conditions with extension possibilities for AFM, SEMPA, FIB, and EBL. This enables in situ SEM and STM imaging to study the sample topography from mm down to 10 pm scale on the same sample spot. Using the electron column as an excitation source for Auger, chemical analysis is possible with sub 10 nm resolution. STM related techniques like STS allow the characterisation of the electronic structure and magnetic imaging using spin polarised STM. Besides the observation of sample properties, the STM+SEM combination also offers unique possibilities for sample modification on the nanoscale, offering both electron beam lithography and STM manipulation under SEM control. Using Ag nanocrystals on Si(111), we demonstrate the capabilities of this approach. The samples were prepared by evaporation of Ag on a clean Si (111) substrate at elevated temperatures. We show SEM and SAM images with a resolution down to 3 nm (SEM), and 10 nm (SAM) respecively allowing for chemical analysis with ultimate resolution. We demonstrate the importance of SEM to select areas of interest, and subsequently position the STM tip to image these areas. STM images with atomic resolution show the surface structure and reconstructions on both the silver crystals and the silicon substrate. The latter shows a @sr@3x@sr@3 reconstruction induced by the silver.

4:00pm **NS1-ThA7 Atomic Level Analysis of Polythiophene by the Scanning Atom Probe***, **O. Nishikawa**, M. Taniguchi, M. Ihara,* Kanazawa Institute of Technology, Japan*; H. Kato, S. Takemura,* Kanto Gakuin University, Japan

Thin films of conductive polythiophene grown by the electrochemical process on silicon and ITO substrates are investigated by utilizing unique capability of the scanning atom probe (SAP). The thickness of the films is 10 to 30 Î¼m and the dopant is BF4-. Since the variation of the field emission current I with the applied voltage V to the polythiophene is related with the work function of the specimen surface, the I-V curves, the F-N plot, were obtained. The slope and intercept of the F-N plots (S-I chart) indicates that the work function does not vary with the synthesizing process and the substrate. The comparison of the S-I chart of CNT, W and Si shows that the work function of the polythiophene is close to that of Si. The variation of the S-I chart with temperature also suggests that the polythiophene films are semi-conductive because the emission current varies with temperature as Si. The SAP analysis was conducted by applying voltage pulses or laser pulses. The mass spectra of the detected ions are closely related with the structure of the polythiophene. The Most abundant ions have the masses 80 to 83 which indicates that these ions are SC4Hn, the basic unit of the polythiophene. The ratio of the number of sulphur atoms to that of carbon atoms is 1 to 4 as expected. The detection of various ions such as C+, C2+ and SC3Hn+ suggests that some areas not polymerized and stay in the graphite like state. All sulphur atoms were found as a clustering atom with carbon and hydrogen such as SC4Hn2+ and SC3Hn+. Since the evaporation field of doubly charged ions is usually higher than that of singly charged ions, the detection of doubly charged cluster ions indicates that the SC4Hn2+ clusters are very stable and the atoms forming the clusters are fairly strongly bound. No oxidation of the polythiophene was noticed.

4:20pm **NS1-ThA8 Probing Ion Transport at the Nanoscale: Time-Domain Electrostatic Force Spectroscopy on Glassy Electrolytes***, **A. Schirmeisen**, A. Taskiran, H. Fuchs, B. Roling, S. Murugavel, H. Bracht, F. Natrup,* University of Muenster, Germany

Ion conducting solid materials play an important role as electrolytes in energy conversion systems, such as batteries and fuel cells, and also in electrochemical sensors. Of particular interest are so-called fast ion conductors with conductivities that are comparable to liquid electrolytes. Currently, a lot of research work is being done in order to find new materials with improved conductivities. For instance, nanostructured materials become more and more technologically relevant. An important prerequisite for further progress in this field is a better understanding of the ion transport mechanisms on microscopic length scales. Up to now, the experimental techniques used for probing the ion transport are mainly macroscopic in nature, e.g. conductivity spectroscopy, tracer diffusion measurements and NMR relaxation techniques. The macroscopic averaging over the motions of all ions in a sample leads to a loss of information making it desirable to develop techniques that are capable of probing the ion transport on nanoscopic length scales. In this contribution, we demonstrate that electrical atomic force microscopy (AFM) techniques yield information about the dynamics of mobile ions in small subvolumes of a sample. In dynamic mode AFM, a voltage is applied between the tip and the sample, at typical tip-sample distances of about 10 nm. In this case, the voltage drop in the sample occurs mainly in a nanoscopic subvolume below the surface. Ionic motions in this subvolume influence the electrostatic forces acting between tip and sample. We record the time dependent evolution of the forces at sample temperatures from 100 K to 600 K, which allows us to extract the activation energy of the ion conduction process. The comparison of macroscopic with our nanoscopic measurements on different solid electrolytes shows that time-domain electrical AFM is capable of probing the ion dynamics and transport in nanoscopic subvolumes of the samples.

5:00pm **NS1-ThA10 Novel MEMS Devices for Accurate Lateral and Normal Force Measurement in AFM***, **P.J. Cumpson**,* National Physical Laboratory, UK, United Kingdom*; J. Hedley,* Newcastle University, UK

The uncertainty in the spring constants of AFM cantilevers is a limiting factor in a wide range of measurements of nanoscale quantities (chemical, electrical, mechanical) at a lateral resolution of 30 nm or below. The tip/cantilever fabrication process suggests that manufacturing cantilevers to the exquisite dimensional accuracy required to produce sufficiently repeatable spring constants will always be a challenge; an easy and accurate calibration method is needed. A number of methods have been suggested for calibrating AFM cantilevers@footnote 1@, all of which have limited accuracy or are difficult to perform. We have developed a novel microfabricated device capable of calibrating AFM cantilevers for normal spring constant@footnote 2@ much more easily. The device consists of a surface micromachined silicon resonator, which can be set into resonance at an amplitude of around 10 nm in vacuum. By applying Doppler interferometry and electrical measurement simultaneously, the spring-constant of the MEMS device can be deduced, to an uncertainty of around ±2%, without physical contact. Here we present a new MEMS device for the first time, specifically designed to make lateral force constant calibration easy and accurate. This presented challenging fabrication and interferometry problems. Nevertheless, it is particularly valuable since few other options exist for quantitative measurement of lateral force. @FootnoteText@ @footnote 1@ N A Burnham et al, Nanotechnology 14 (2003) 1-6.@footnote 2@ P J Cumpson and J Hedley, Nanotechnology 14 (2003) 1279-1288.

Nanometer-scale Science and Technology
Room 213D - Session NS2-ThA

Nanowires II

Moderator: S.-T. Lee, City University of Hong Kong, China

2:00pm **NS2-ThA1 Gaede-Langmuir Award Presentation: Ultra-high Vacuum Electron Microscopy for Surface Analysis and Nanomaterials***,* **INVITED**

Nanostructures are investigated increasingly by ultra-high vacuum (UHV) electron microscopy in the last decades. In recent years scanning tunneling microscope (STM) and/or atomic force microscope (AFM) is incorporated in UHV electron microscope apparatus to study not only structures but also properties in-situ. Also a great advance in the optics of the electron microscope, aberration free lens, allows us to image individual atoms (or atomic columns) within nanostrucutres. I present recent development of our UHV high-resolution electron microscopy that has an aberration free lens and a scanning probe microscope, and results on conductance quantization of metal nanowires and forces acting on the free-standing nanowire that spans between electrodes

2:40pm **NS2-ThA3 VLS Epitaxy of Si Nanowires: Kinetics and Morphology***, **T. Clement**, J.L. Taraci, J.W. Dailey, D.J. Smith, J. Drucker, S.T. Picraux,* Arizona State University

The high aspect ratios and novel electronic and chemical properties of silicon nanowires have made them increasingly interesting for applications ranging from flexible electronics to chemical sensors to microfluidic surfaces. However the mechanisms behind vapor-liquid-solid (VLS) crystal growth have received only limited attention since the seminal work of Wagner for whisker growth more than 30 years ago.@footnote 1@ Here we study the VLS kinetics and growth modes dominating CVD grown Si nanowires (SiNWs) as a function of growth pressure and temperature. In contrast to our previous studies of Ge nanowires, we observe SiNW growth throughout a wide range of pressures and temperatures. Au nanodots with a nominal thickness of 2.5 nm and average lateral separation of 30 nm are evaporated in UHV on hydrogen terminated Si(111) and Si(100) surfaces; these Au nanodots function as the seeding species for VLS nanowire growth. Subsequent growth using disilane (Si@sub 2@H@sub 6@) gas at pressures ranging from 1x10@super -2@ to 1x10@super -6@ Torr and temperatures ranging between 300°C and 700°C produces highly uniform SiNW structures at low temperatures and unstable structures at higher temperatures, specifically kinks and nonuniformity in SiNW diameter. The initiation of nanowire growth is a nucleation-limited process, and we also report on new in situ optical scattering studies of SiNW nucleation times. Finally, characterization via field-emission SEM, RBS, and TEM will establish the SiNW growth rate dependence on substrate temperatures and pressures. Examples of the dramatic superhydrophobic and superhydrophilic behavior of functionalized SiNW surfaces will be given. @FootnoteText@ @footnote 1@ R.S. Wagner, in Whisker Technology, Levit, A.P. ed, (Wiley-Interscience, New York, 1970) pp 47-119.

3:00pm **NS2-ThA4 Growth Of ZnO Nanowires and Their Applications in Dye Sensitized Solar Cells***, **J.B. Baxter**,* University of California Santa Barbara*; M. Reichman,* University of Texas-Austin*; E.S. Aydil,* University of California Santa Barbara

ZnO is a wide band gap semiconductor (Eg = 3.37 eV) with applications in UV optoelectronics, varistors, piezoelectronics, and photovoltaics.

Nanostructured ZnO can enable applications that require high semiconductor surface area such as sensors and dye sensitized solar cells. We have grown single crystal ZnO nanowires ~80 nm in diameter and several microns long by chemical vapor deposition (CVD) using the organometallic precursor zinc acetylacetonate (Zn(acac)@sub2@) in the presence of oxygen. Dense arrays of ZnO nanowires exhibit large surface areas and can be grown on various oxide substrates, making them suitable as the mesoporous semiconductor in dye sensitized solar cells. Single crystal ZnO nanowires offer improved conduction pathways compared to sintered nanoparticles used currently, where electron transport occurs by a hopping mechanism. The surface area for dye adsorption can be increased significantly by extending the growth time to allow for the nucleation and growth of smaller secondary nanowires from the primary nanowires, improving current densities in the cells. We have used these types of nanowires to produce initial solar cells with short circuit current densities of 75 µA/cm@super2@, open circuit voltages of 0.63 V, and fill factors of 39 % when illuminated with 100 mW/cm@super2@ simulated solar light. A limitation of the initial solar cells is poor light harvesting, with less than 10% of incident light absorbed by the dye. We are currently investigating methods for seeding nanowire growth to improve the nucleation density, which will increase nanowire surface area and dye adsorption. Transport properties of the nanowires can be significantly enhanced by treatment in hydrogen plasma at room temperature. H atoms passivate defects and increase conductivity by increasing carrier densities. H exposure improves the UV photoluminescence of the nanowires and both the fill factor and the open circuit voltage of the solar cells.

3:20pm **NS2-ThA5 Progress Towards Silicon Nanowire-based Complementary Logic**, ***T.S. Mayer***, *Y. Wang, T.-T. Ho, K.-K. Lew, L. Pan, E.C. Dickey, J.M. Redwing,* Penn State University **INVITED**

There has been considerable interest in bottom-up assembly of semiconductor nanowires for their application in future logic, memory, and sensor circuits. In this talk, we will present results of recent research showing that p- and n-type dopants can be intentionally incorporated into silicon nanowires (SiNWs) during template-directed vapor-liquid-solid (VLS) growth to produce complementary field effect devices. In this work, Au metal particles electrodeposited within 80-nm diameter pores of anodized alumina templates serve to catalyze SiNW growth at temperatures of 500° C using 10% silane (SiH@sub 4@) in H@sub 2@ as the silicon gas source, trimethylboron (TMB) as the p-type dopant, and phosphine (PH@sub 3@) as the n-type dopant. Transmission electron microscopy (TEM) studies of individual SiNWs show that approximately two-thirds of the SiNWs are single crystal, while the remaining one-third are bicrystals. Additionally, the surfaces of all of the p- and n-type SiNWs investigated were free of amorphous layers that were observed previously when diborane was used as a p-type dopant gas. Secondary ion mass spectroscopy (SIMS) on bundles of SiNWs indicate that B- and P-concentrations increase with increasing TMB:SiH@sub 4@ or PH@sub 3@:SiH@sub 4@ gas ratios between 10@super -5@ and 10@super -2@, and can exceed 10@super 19@ cm@super -3@ for the highest gas ratios investigated. Gate-dependent conductance measurements of individual B- and P-doped SiNWs show complementary characteristics that are consistent with depletion mode device operation, where the threshold voltage is adjusted by changing the dopant:SiH@sub 4@ gas ratio during VLS growth. Independent measurements of four-point resistivity also show a clear decrease in resistivity with increasing TMB:SiH@sub 4@ or PH@sub 3@:SiH@sub 4@ gas ratios. These results confirm that p- and n-type dopants can be effectively incorporated during SiNW synthesis to produce complementary field effect devices in the same material system.

4:00pm **NS2-ThA7 The Role of Electrodeposited Metal Nanowires in Gas Sensing**, ***B.J. Murray***, *E.C. Walter, R.M. Penner,* University of California, Irvine

It in unclear what role, if any, metal nanowires have to play in chemical sensing. While the literature is ripe with examples of sensors based on semiconductor nanowires, there have been very few examples using metal nanowires. For these investigations - silver, copper, gold, and platinum nanowires were prepared by Electrochemical Step Edge Decoration (ESED) on a graphite surface. These nanowires were polycrystalline, consisted of a 1-D array of fused particles 50 nm to 950 nm in diameter, and had lengths of 100 µm or more. The resistance of these metal nanowires was probed as a function of the concentration of a chemisorbing gas. Upon exposure to ammonia (NH@sub 3@), arrays of these "fused particle" wires showed a resistance increase, @DELTA@R/R@sub 0@, that was fast, large (up to 1,000%), and reversible. Compared to literature on thin metal film sensors, the response of these nanowire arrays was much larger than expected. We propose that the elements responsible for this response were concentrated at a small minority of locations along axis of the wires. This proposed model, the Chemically Responsive Interparticle Boundary (CRIB) model, will be discussed. Finally, the chemical structure of these elements has been investigated to determine the role, if any, of air oxidation on sensor function.

4:20pm **NS2-ThA8 1-D Metal Oxide Sensor and Catalyst: the Comparative Study of Pristine and Surface Doped Individual Nanowire**, *A.A. Kolmakov,* University of California, Santa Barbara*; S.V. Kalinin,* Oak Ridge National Laboratory*; Y. Lilach,* ***M. Moskovits,*** University of California, Santa Barbara

We investigated transport properties of individual metal oxide single crystal nanowires and nanobelts operating in high vacuum and under â?oreal worldâ? conditions for sensing and catalysis applications. Using impedance measurements under different gas environment in conjunction with scanning probe microscopy we were able to determine the major factors contributing to charge transport in nanowire. We found that when nanowire radius is comparable with its Debye length, the adsorption/desorption of donor/acceptor molecules on the surface of the nanowire and in its proximity alters the bulk electron density inside the nanowire what sensitively modulates conductivity of the nanowire. In vivo conductometric measurements on individual nanowire during its surface doping with metal particles reveals the formation of nano-Schottky barriers which drastically enhance of the reactivity/selectivity of the nanowire as gas sensors and catalyst.

4:40pm **NS2-ThA9 Thermoelectric Nanowire Arrays for Waste Heat Conversion**, ***E. Menke***, *R.M. Penner,* University of California at Irvine

No longer relegated to specialized roles like powering satellites, thermoelectric materials are garnering interest for more mundane uses like solid-state refrigerators and collecting waste heat in automobiles. A number of research groups are currently working on a variety of methods to improve the efficiency of thermoelectric materials. Our attempts to create more efficient thermoelectric devices have focused on fabricating arrays of high aspect ratio nanowires of bismuth telluride, presently the best conventional thermoelectric material for room temperature applications. I will present our method for preparing bismuth telluride and doped bismuth telluride nanowires on highly oriented pyrolytic graphite via electrochemical step-edge decoration. This will be followed by the characterization of these nanowires by scanning electron microscopy, x-ray diffraction, and energy dispersive x-ray analysis. Finally, I will end by briefly discussing our attempts to measure the thermoelectric figure of merit for these nanowires.

5:00pm **NS2-ThA10 Devices Formed Using Deposited Polymeric Nanofibers**, *J. Kameoka,* Cornell University*; H. Liu,* Cornell Univeristy*; D. Czaplewski, R. Mathers, S. Verbridge, G. Coates,* ***H.G. Craighead***, Cornell University

We have used deposited polymer nanofibers for the formation of electrical, optical and mechanical devices. We used a microfabricated tip as a controlled scanning source for electrostatically driven deposition of oriented nanofibers and for interfacing the fibers to lithographically defined surface structures. Because of the ability to deposit these materials as individual oriented fibers with diameters in the range of 50 nm to ~1µ, they can be utilized in new device architectures. In this talk we describe the use of the deposited polymer nanofibers as chemical sensors and as templates for the formation of mechanical and nanofluidic devices composed of inorganic materials. Utilizing the properties of a conducting polyaniline polymer we have formed ammonia sensors comprising a single oriented fiber deposited on gold electrodes. We created mechanical devices such as silicon nitride mechanical oscillators with dimensions on the order of 100 nm, formed using deposited poly(methylmethacrylate) fibers. The oscillators were defined in a silicon nitride layer by using the fiber as a mask for reactive ion etching, followed by removal of a sacrificial underlying layer. After releasing the devices, the frequencies of the modes of oscillation of the beams were determined by laser interference techniques. We fabricated nanofluidic channels of elliptical cross-section, without the use of high resolution lithography. The sacrificial template fiber consisted of a heat-decomposable polycarbonate that was deposited on a substrate and encapsulated by a spin-on glass. The channels were formed by thermal removal of the sacrificial polymer nanofibers. The oriented nanofiber deposition method, used in these experiments, offers an approach for the rapid formation of self-assembled nanoscale devices, connected to microfabricated structures, which would be difficult to form using a completely self-assembled or completely lithographic approach.

Organic Films and Devices
Room 304C - Session OF+EM-ThA

Molecular and Organic Films and Devices - Optoelectronic

Moderator: T.U. Kampen, Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany

2:40pm **OF+EM-ThA3 Plasma Damage-Free Deposition of Metal and ITO Electrodes on Organic Light Emitting Diodes by Using Mirror Shape Target Sputtering(MSTS)***, **H.-K. Kim**, D.-G. Kim, K.A. Lee, M.-S. Huh, S.H. Jeong, K.I. Kim,* Samsung SDI, Korea

We report a successful fabrication of plasma damage-free organic light-emitting diodes (OLED) by using a mirror shape target sputter (MSTS) technique. Compared to leakage current (1*10@super-1@ ~10@super-2@mA/cm@super2@ at -6V) of the OLED consisted of Al cathode grown by conventional DC magnetron sputtering, that of the OLED with an Al cathode grown by MSTS shows much lower leakage current at reverse bias (1*10@super-5@ mA/cm@super2@ at -6V), indicative of no plasma damages. Therefore, the MSTS technique is expected to be useful in plasma damage-free and low temperature deposition technique for top and bottom-emitting OLEDs and flexible OLED. Possible mechanism is given to explain plasma damage free deposition of the metal and ITO electrodes by using current-voltage characteristics, SEM, AFM, XRD, and TEM examinations.

3:00pm **OF+EM-ThA4 Magnetic Field Effects in Transient Electroluminescence (EL) from Alq@sub 3@/NPB Bi-layer Organic Light Emitting Diodes***, **J. Wilkinson**, A.H. Davis, K. Bussmann, J.P. Long,* Naval Research Laboratory

The long electron spin lifetimes commonly found in organic materials make organic light emitting diodes (OLEDs) potential candidates for spin-injection controlled light sources. However, direct-current measurements of electroluminescence (EL) in OLEDs with non-magnetic electrodes (i.e. with no spin injection) show a variation in EL with applied magnetic field that must be understood. For example, EL can increase by as much as 6% around 0.1 Tesla (T) before decreasing by up to 20%, at 2 T.@footnote 1@ This shows that magnetic field effects are not due to spin injection, but are an intrinsic property of the light emission process. To probe the causes of these processes, we have performed sensitive transient EL experiments in the low-field regime (H = 80 mT) where the magnetic field enhances EL. The OLED is driven with rectangular voltage pulses producing a temporal response in EL with features down to the system resolution of 70 ns. The time-dependent magnetic field effect, defined as @DELTA@EL/EL = [EL(H) - EL(0)]/EL(0) increases EL by 6% for a 3.6 V drive at room temperature, as in direct-current measurements. But in addition @DELTA@EL/EL has interesting transient behavior when the device is first turned on, and again after the drive pulse is turned off during a long-lived delayed EL signal. As the device turns on, @DELTA@EL/EL doubles relative to its steady state value, which it attains on the microsecond timescale. Immediately after device turn-off, a long-lived increase in @DELTA@EL/EL is detected as well. The measured tendency for the magnetic field enhancement of EL to decrease as the transient EL increases is consistent with drive-dependent measurements. Together, these experiments indicate that high concentrations of non-equilibrium carriers or excitons interfere with the magnetic enhancement process. @FootnoteText@ @footnote 1@ A.H. Davis and K. Bussmann, Organic Light-Emitting Materials and Devices VII, eds. Z.H. Kafafi and P.A. Lane, 5214, 57-63 (2004).

3:20pm **OF+EM-ThA5 Molecular N-Type Doping of NTCDA by Pyronin B***, **C.K. Chan**, A. Kahn,* Princeton University

Molecular n-type doping of 1,4,5,8-naphthalene tetracarboxylic dianhydride (NTCDA) by pyronin B (PyB) is observed using ultraviolet photoemission spectroscopy (UPS) and inverse photoemission spectroscopy (IPES). The leuco form of the dopant molecule is prepared in situ by heating the stable PyB chloride salt until sublimation@footnote 1@. UPS of the neat PyB film shows that the highest occupied molecular orbital (HOMO) of the material is 5.69eV below the vacuum level (E@sub vac@), whereas the lowest unoccupied molecular orbital (LUMO) of NTCDA is at 4.08eV below E@sub vac@, as determined by IPES. Despite this relatively large energy difference between donor and electron transport states, the deposition of small amounts (<2Å) of PyB on pristine NTCDA films leads to a shift of the HOMO away from the Fermi-level by nearly 0.20eV, indicative of n-type doping of NTCDA by PyB and in agreement with the results of Werner et al.@footnote 1@. Interface and bulk energy levels of co-evaporated films show similarly efficient doping. Current-voltage measurements on doped NTCDA diode devices will also be presented. @FootnoteText@ @footnote 1@ A. G. Werner, F. Li, K. Harada, M. Pfeiffer, T. Fritz, and K. Leo, Appl. Phys. Lett. 82, 4495 (2003).

3:40pm **OF+EM-ThA6 Electrical Doping of Poly(9,9-dioctylfluorenyl-2,7-diyl) with Tetrafluoro-Tetracyanoquinodimethane by Solution Method***, **J.H. Hwang**, A. Kahn,* Princeton University

Electrical doping of organic materials has received attention for enhancing carrier injection and lowering drive voltages. We investigate here p-type doping of poly(9,9-dioctylfluorenyl-2,7-diyl) (PFO) with tetrafluorotetracyanoquinodimethane (F4-TCNQ) using a solution method. Doped and undoped films were compared using ultraviolet photoelectron spectroscopy (UPS) and current-voltage (I-V) measurement. Undoped PFO was prepared from 0.1wt% of tetrahydrofuran (THF) and p-xylene. For doped PFO, 5% of F4-TCNQ relative to each repeat unit of PFO was added to each solution. Undoped and doped films (~100Å thick) were spun on ITO or Au substrates in nitrogen, annealed in nitrogen at 50°C to remove residual solvent, and loaded without ambient exposure in an ultra-high vacuum chamber. UPS spectra were recorded for each film. The energy of the highest occupied molecular orbital (HOMO) was measured with respect to the Fermi level (E@sub F@). The ionization energy of PFO, determined as the difference between vacuum level (measured from the onset of photoemission) and HOMO, was found to be 5.75 eV, which is ~0.5 eV larger than the electron affinity of F4-TCNQ (5.24eV)@footnote 1@.In spite of the fact that this difference is significantly larger than for ZnPc (0.04 eV)@footnote 1@ and a-NPD (0.28 eV)@footnote 2@, F4-TCNQ p-dopes the polymer. EF-HOMO is 1.1 eV and 1.4 eV for undoped PFO on Au and ITO, respectively, and drops by 0.2 eV for PFO:F4-TCNQ, showing a shift in the expected direction for p-doping. We also performed I-V measurements on Au/1200Å PFO/ITO, which show an order of magnitude increase in current in doped PFO, consistent with higher conductivity and/or lowering of the hole-injection barrier. These measurements show that electron transfer from host to dopant occurs and produces p-type doping. @FootnoteText@ @footnote 1@ W. Gao, A. Kahn, Appl. Phy. Lett., 79, 4040 (2001)@footnote 2@ W. Gao and A. Kahn, J. Appl. Phys. 94, 359 (2003).

4:00pm **OF+EM-ThA7 Negative Capacitance in Hetero-Layered Organic Light Emitting Diodes***, **L.S.C. Pingree**, B.J. Scott, T.J. Marks, M.C. Hersam,* Northwestern University

Negative capacitance (NC) has been measured by impedance spectroscopy and correlated with time domain waveforms in ITO/NBP/Alq@sub 3@/Al OLED macroscopic devices. In addition, this behavior has been measured by Nanoscale Impedance Microscopy@footnote 1@ on 8 µm x 8 µm microscopic OLED devices. Beyond providing evidence of the scaling of NC, this AFM based technique provides spatially resolved capacitance variations in these structures. Due to the field dependent mobility of the charge carriers, and their subsequent dependence upon both bias and space charge, a slow rise time (t@sub R@) in the current response is detected when a step voltage is applied to the OLED. Such behavior is typical of a NC impedance response@footnote 2@. The typical t@sub R@ varies from 100 ms at 1 volt to 15 ms at 10 volts for electrons, and 100 ms at 1 volt to 1 ms at 10 volts for holes. The onset of NC in the frequency domain correlates strongly with the hole t@sub R@, and the corresponding frequencies are exponentially dependent upon the applied bias. These results agree with the exponential dependence of mobility upon applied field given by Poole-Frenkel theory. Also, the variation between the carrier rise times suggests that Richardson-Schottky injection dominates electron flow. Correlation of the data with device physics implies that NC behavior is hole dominated since the flow of electrons is modulated solely by holes trapped at the Alq@sub 3@/NPB interface, whereas holes respond to both bias and space charge. Additionally, temporal variations in the behavior of light emission as a function of frequency were acquired though the use of a dual lock-in technique. @FootnoteText@ @footnote 1@R. Shao et. al. Appl. Phys. Lett. 82 1869 (2003).@footnote 2@M. Ershov et. al. IEEE Trans. Elect. Dev. 45 2196 (1998).

4:20pm **OF+EM-ThA8 Electronic Structure and Molecular Orientation of Conducting Polymer Films Produced via Surface Polymerization by Ion Assisted Deposition***, **S. Tepavcevic**, Y. Choi,* University of Illinois at Chicago*; M. Bissen, D. Wallace,* University of Wisconsin-Madison*; L. Hanley,* University of Illinois at Chicago

Conducting polymer films are grown by mass-selected, hyperthermal organic cations coincident on a surface with a thermal beam of organic monomers, in a process termed surface polymerization by ion assisted deposition (SPIAD).@footnote 1,2@ SPIAD is applied here to create polymer films from thiophene ions and either @alpha@-terthiophene neutrals (3T SPIAD) or p-terphenyl neutrals (3P SPIAD). Mass spectrometry and x-ray photoelectron spectroscopy (XPS) verify the polymerization of both 3T and 3P SPIAD films. The electronic structure and molecular orientation of these films are probed by valence band XPS, ultraviolet photoelectron spectroscopy (UPS) and polarized near-edge x-ray absorption fine structure spectroscopy (NEXAFS). Valence band XPS and UPS of the 3T SPIAD films produced with 200 eV ions and an ion/neutral ratio 1/150 display similar spectral features as polythiophene films prepared electrochemically. A new state is observed 1 - 3 eV below the Fermi level in the 3T SPIAD film spectra which is not observed in films prepared by evaporation of 3T. This new state is attributed to an extended @pi@* bonding band along the conjugated aromatic chain of the polymerized 3T. Carbon K-edge NEXAFS probes the unoccupied @pi@* and @sigma@* bands of 3T SPIAD films which appear similar to those of the evaporated 3T film. Polarized NEXAFS show that the 3T SPIAD film is at least partially oriented with their molecular axes close to the normal of the substrate surface. The 3P SPIAD film prepared at 200 eV with an ion/neutral ratio 1/100 display more electron delocalization over the @pi@* bonding band compared with the 3P evaporated film. Polarized NEXAFS shows that as little or no orientation in the 3P SPIAD film, in contrast to the highly oriented 3P film. @FootnoteText@ @footnote 1@S. Tepavcevic, Y. Choi, and L. Hanley, J. Amer. Chem. Soc. 125 (2003) 2396. @footnote 2@Y. Choi, S. Tepavcevic, Z. Xu, and L. Hanley, Chem. Mater. (2004) in press.

Plasma Science and Technology
Room 213A - Session PS-ThA

Plasma-Surface Interaction

Moderator: G.F. Franz, University of Applied Sciences, Germany

2:00pm **PS-ThA1 A Comprehensive Study of Gas Phase and Plasma-Surface Interactions of Depositing Fluorocarbon Plasma Systems***, **I.T. Martin**, E.R. Fisher,* Colorado State University

A thorough investigation of the gas-phase chemistry, plasma-surface interactions, and surface properties of deposited materials has been performed for C@sub 3@F@sub 8@ and C@sub 4@F@sub 8@ plasmas. OES-actinometry, LIF and MS were used to study the plasma gas phase. OES quantifies excited state species in these systems, whereas LIF measurements provide relative densities of ground state CFx species as a function of applied rf power (P) and pressure. CF LIF excitation spectra were used to measure CF rotational temperatures (@Theta@@sub R@) as a function of P and pressure: @Theta@@sub R@(CF) in C@sub 4@F@sub 8@ plasmas is approximately constant over a range of P and pressure, whereas it increases with P in the C@sub 3@F@sub 8@ systems. MS data identify nascent ions and measure ion energy distributions. Plasma-surface interactions of CFx species were investigated using our Imaging of Radicals Interacting with Surfaces (IRIS) molecular beam apparatus. CF@sub 2@ surface production was characterized during C@sub 3@F@sub 8@ and C@sub 4@F@sub 8@ plasma processing of Si via a scattering coefficient, S(CF@sub 2@), the ratio of CF@sub 2@ molecules scattering from the surface relative to those in the molecular beam. S(CF@sub 2@) values>1 were measured during the deposition of amorphous fluorocarbon (FC) materials. This net surface production of CF@sub 2@ suggests that CF@sub 2@ is not a deposition precursor in these FC systems. Charged species contribute to CF@sub 2@ surface production, as demonstrated by the decrease in S(CF@sub 2@) measured under ion-limited conditions. A notable result of this work is the positive correlation between S(CF@sub 2@) and %-crosslinking measured by XPS in the deposited FC materials. Optimized FC materials were used in several applications, including the production of micropatterned surfaces used in cell growth studies, and the modification of microfluidic devices. The performance of our FC materials in these applications will be discussed.

2:20pm **PS-ThA2 Mechanisms of Etching in the Presence of Depositing Species: Molecular Dynamics Simulations of Silicon Etching in Fluorocarbon Plasmas***, **J.J. Vegh**, D. Humbird, D.B. Graves,* University of California, Berkeley

The fundamental mechanisms of plasma etching in the presence of depositing species, a very common situation in industrial practice, remains poorly understood at the atomistic level. Recent MD simulations of silicon etching in the presence of small FC ions and neutral radicals, F atoms, and Ar@super +@ have consistently failed to reproduce experimental observations of simultaneous Si etching and the presence of relatively thick FC film on the surface. Simulations of FC film formation alone, without Si etching, can easily be observed with small unsaturated FC ions at energies below about 100 eV, and thermal CF and CF@sub 2@ are observed to deposit alone or in the presence of low energy ion bombardment (@<=@50 eV). Si etching is observed in the presence of higher energy ions, especially Ar@super +@, and most readily in the presence of thermal F. However, the combination of significant Si etch, coupled with dominant FC signal in simulated surface XPS measurements, has proven elusive using only small FC species. Even at relatively high neutral to ion ratio (e.g. 90:9:1 CF/F/Ar@super +@), only a thin FC film develops during Si etch, and the XPS is dominated by the C-C/Si peak. We conclude that simultaneous FC film and Si etch requires heavier, unsaturated FC neutrals and/or ions. These large, polymeric species are created by ion impact or neutral F attack within a deposited FC film. In other words, the FC film can be etched in the form of large products that redeposit on the surface to maintain the film. We demonstrate that simultaneous FC film and Si etch requires that the FC film have minimal cross-linking and be relatively weakly bound to the surface. We highlight the role of ion impact in locally removing substantial amounts of FC film material, exposing the underlying Si to etch species.

2:40pm **PS-ThA3 Deposition and Composition of Polymer Films in Fluorocarbon Plasmas: CW and Pulsed Systems@footnote 1@***, **K. Rajaraman**, M.J. Kushner,* University of Illinois at Urbana-Champaign

Fluorocarbon plasma etching is the primary method to obtain selectivity between dielectrics. Optimization of this etching technique becomes more critical as dielectrics thin. To first order, etch rates depend on thickness of the polymer layer, which controls the energy of ions striking the dielectric surface. However, the composition of the polymer determines the rate of deposition and sputtering of the film, as well as the rate of reaction of the polymer with the underlying dielectric. To address this compositional dependence, a surface chemistry model has been developed to resolve the polymer at a mesoscale level by treating CFx sites distinctly. In this manner, the fractional composition of the polymer film on a bond-to-bond basis can be resolved. This surface model was interfaced with a zero-dimensional plasma kinetics model (GLOBAL_KIN) and a 2-dimensional plasma equipment model (HPEM). Simulations were performed using the ICP reactor geometry and conditions from Li et al.@footnote 2@ We will discuss results for film compositions using different fluorocarbon gas chemistries (e.g., M/O@sub 2@/Ar, M = C@sub 2@F@sub 6@, CHF@sub 3@, c-C@sub 4@F@sub 8@). Due to the change in the pathways for generation of major free radicals, the fluorocarbon films formed in the chemistries investigated are qualitatively different, and to some degree reflect the fragmentation pattern of the feedstock gases. Changes in Ar concentration affect the amount of sputtering of the fluorocarbon films, and hence the film thickness. The consequences of pulsing the plasma on the fluorocarbon film structure will also be discussed. @FootnoteText@ @footnote 1@ Work supported by SRC and NSF. @footnote 2@ Li et al., J. Vac. Sci. Technol. A 20, 2052 (2002)

3:00pm **PS-ThA4 Dangling Bond Creation and Annihilation during Plasma Processes Studied by In-situ ESR Technique***, **S. Yamasaki**,* AIST, Japan*; K. Ishikawa,* Tohoku University, Japan **INVITED**

To understand the surface chemical reactions of plasma processes, various probes have been introduced for monitoring. Defect creation and annihilation during plasma processes, whether at surface or in bulk, play an essential role in determining final device performances and chemical reactions. If one can directly observe the creation and annihilation of dangling bond (db) centers and those dynamic changes of bonding configurations during plasma processes in real-time, it will give important information for improvement of plasma processes. In this talk we introduce in-situ ESR measurements [1,2], detecting surface defects during H2 and Ar plasma treatments on hydrogenated amorphous silicon (a-Si:H) and in-line ESR measurements during fluorocarbon gas etching processes of SiO2. From these experimental results we report how the plasma species affect surface defect structure and discuss the surface chemical reactions. [1] K. Ishikawa, et al., Appl. Phys. Lett. 81, 1773 (2002). [2] S. Yamasaki, et al., Appl. Phys. Lett. 70, 1137 (1997).

3:40pm **PS-ThA6 NH@sub x@ Radical Densities and Plasma Chemistry in a Remote Ar-NH@sub 3@-SiH@sub 4@ Plasma for Silicon Nitride Deposition***, **P.J. van den Oever**,* Eindhoven University of Technology, The Netherlands, Netherlands*; J.H. van Helden, R. Engeln, D.C. Schram, M.C.M. van de Sanden, W.M.M. Kessels,* Eindhoven University of Technology, The Netherlands

Although plasma deposited amorphous silicon nitride (a-SiN@sub x@:H) has widespread applications in industry, the exact growth mechanism of these films from NH@sub 3@-SiH@sub 4@ plasmas remains unclear. For example, the role of silane radicals, ammonia radicals, and possibly aminosilane radicals in the growth process is still not resolved. To obtain insight into the role of the various radicals in the plasma we have carried out absolute density measurements of NH and NH@sub 2@ radicals in a remote Ar-NH@sub 3@ and Ar-NH@sub 3@-SiH@sub 4@ plasma. The radicals have been detected by means of the cavity ringdown spectroscopy (CRDS) technique probing NH and NH@sub 2@ electronic transitions at ~597 and ~335 nm, respectively. The absolute densities obtained range from 10@super 10@ to 10@super 12@ cm@super -3@ depending on the NH@sub 3@ flow, downstream axial position, and the presence and flow of SiH@sub 4@. The kinetic gas temperature determined from Doppler broadening of the absorption lines is ~1500 K, in agreement with previous measurements. For the Ar-NH@sub 3@ plasma an increase of the NH and NH@sub 2@ density with the NH@sub 3@ flow has been observed. Analysis of the data on the basis of the reaction rates proposed in literature, suggests a considerable regeneration of NH@sub 3@ from its dissociation products. This possibly explains the high NH@sub 3@/SiH@sub 4@ ratio that is necessary to obtain a sufficiently high N/Si ratio in films deposited from Ar-NH@sub 3@-SiH@sub 4@ plasmas. The addition of SiH@sub 4@ decreases the NH@sub 2@ density in the Ar-NH@sub 3@-SiH@sub 4@ plasma and at low NH@sub 3@ flows even no NH@sub 2@ is observed. To understand these trends, which can originate both from plasma and surface processes, the NH density is currently investigated under the same plasma conditions. From a comparison of the results with those obtained from a simple plug-down model, insight into the key reactions in the Ar-NH@sub 3@-SiH@sub 4@ plasma is obtained.

4:00pm **PS-ThA7 First-Principles Analysis of Precursor-Surface Interactions Relevant to Plasma Deposition of Silicon Thin Films***, **T. Bakos,*** University of Massachusetts, usa*; D. Maroudas,* University of Massachusetts

Plasma-enhanced chemical vapor deposition is used widely for growing hydrogenated amorphous silicon (a-Si:H) thin films for electronic, optoelectronic, and photovoltaic applications. Plasma deposited film properties, such as H content, crystallinity, and surface roughness, depend on the identities and fluxes of reactive radicals impinging on the deposition surface and on the corresponding radical-surface interaction mechanisms. In this presentation, we report results of first-principles density functional theory (DFT) calculations that elucidate the reaction pathways and energetics of key reactions with the H-terminated Si(100)-(2x1) surface of the SiH@sub 3@ radical, the dominant precursor for deposition of device-quality a-Si:H films. In particular, we have found that SiH@sub 3@ can insert into surface Si-Si dimer bonds, abstract H from surface Si atoms through an Eley-Rideal (ER) mechanism and passivate surface dangling bonds in exothermic and barrierless reactions. In all of these cases, we have determined the optimal reaction pathways and the corresponding transition states based on accurate, well-converged total-energy calculations and implementing the nudged elastic band method. The theoretically predicted energetics of radical insertion, H abstraction, and passivation reactions are consistent with the experimentally observed temperature independence of the SiH@sub 3@ surface reactivity during plasma deposition of a-Si:H films. In addition to the ER mechanism, we have identified a Langmuir-Hinshelwood mechanism of surface H abstraction with a moderate energy barrier that may be responsible for reducing the H content of films deposited at high temperatures. Reactions similar to those analyzed by DFT on the Si(100)-(2x1):H surface also are observed in molecular-dynamics simulations of a-Si:H thin film growth. Therefore, our electronic-structure analysis also can be considered as representative of surface reactions occurring on a-Si growth surfaces.

4:20pm **PS-ThA8 Uniformity Study in Large-Area Showerhead Reactors***, **R. Sobbia**, L. Sansonnens,* Ecole Polytechnique Fédérale de Lausanne (EPFL), Switzerland*; J. Bondkowski,* UNAXIS France SA, France

Large area plasma enhanced chemical vapour deposition of thin films such as silicon nitride or amorphous silicon is widely used for thin film transistor fabrication in the flat panel display industry. A numerical three dimensional model to calculate the deposition uniformity over the whole electrode surface for RF rectangular showerhead reactors powered at 13.56 MHz is presented. The simulation tool is a commercially-available finite-volume software (CFDRC ACE+) which solves the multi-species, multi-reaction chemistry in capacitively coupled plasma. In order to simplify the three dimensional geometry, the injected gas flow distribution across the showerhead is calculated separately and introduced as volumetric source terms for the gas flow and species continuity equations via a dynamic library coupled with the main Solver. The model is applied to the particular case of silicon nitride deposition and the results are compared with uniformity profiles obtained in an industrial PECVD reactor. Perturbations due to reactor edges together with non-uniform distribution of voltage, gas flow and chemical species are investigated as possible sources of the inhomogeneity of the thin-film.

4:40pm **PS-ThA9 Validity of Binary Collision Theory in Ion-Surface Interactions at 50-500 eV***, M. Gordon, **K.P. Giapis,*** California Institute of Technology

Ion-surface interactions in the 50-500 eV regime have become increasingly important in plasma processing. Profile evolution simulations rely on the binary collision approximation (BCA) to estimate the energy of scattered ions. Concerns exist in literature about the validity of the BCA theory at low impact energies because peculiarities are frequently seen in the scattered ion energy distribution. Sub-surface processes, multiple bouncing, and super-elastic phenomena have all been hypothesized. This talk will explore the usefulness of BCA theory in predicting energy transfer during ion-surface collisions in the 50-500 eV energy range. Well-defined beams of rare gas ions (Ne, Ar) were scattered off semiconductor (Si, Ge) and metal surfaces (Al, Mg, Ti, Ag, Au, Ni, Ga) to measure energy loss upon impact. The ion beams were produced from a floating ICP reactor coupled to a small accelerator beamline for transport and mass filtering. Exit energies were measured using a 90 deg electrostatic sector coupled to a quadrupole mass filter with single ion detection capability. Although the BCA presents an over-simplified picture of the collision process, our results demonstrate that it is remarkably accurate in the 50-500 eV range for a variety of projectile-target combinations. However, large deviations from BCA exist for combinations where electron promotions may occur during the hard collision. We find that to be the case for Si, Al, and Mg at energies greater than 500 eV. The promotion occurs at a target-dependent threshold energy and is surface mediated. Further, doubly-charged projectiles maybe generated during the hard collision at the same energy threshold. The implications of these findings for profile evolution during plasma etching will be discussed.

5:00pm **PS-ThA10 Molecular Dynamics Simulation for Physical Sputtering and Deposition of Pt and Au Films***, K. Ito,* Kyoto University, Japan*; H. Yamada,* National Institute of Advanced Industrial Science and Technology (AIST), Japan*; **S.H. Hamaguchi**,* Osaka University, Japan, Japan

Platinum (Pt) is often used as a material of choice for electrodes of submicron-scale capacitors in Dynamic Random Access Memory (DRAM) and other semiconductor devices. Gold (Au) is also used in various electronics applications due to its high conductivity and chemical stability. Since micron/sub-micron-scale etching of noble metals such as Pt and Au in semiconductor applications is usually done mostly by physical sputtering, a better understanding of the nature of beam surface interaction between non-reactive atoms and Pt/Au films may facilitate the development of better noble metal dry etching processes with higher controllability of micro-scale feature profiles. For this purpose, we have used molecular dynamics (MD) simulations to study Ar or Pt beam interaction with Pt substrates and also Ar or Au beam interaction with Au substrates, using classical inter-atomic potential functions based on the Embedded Atom Method (EAM). Especially of interest are estimates of sputtering yields/deposition rates of such processes as functions of beam energies and beam injection angles obtained from MD simulations. Some of the simulation results are in good agreement with known experimental results whereas others are qualitatively different from experimental observations although there have not been many beam experiments in the relatively low energy range that we are interested in. In this presentation, we shall present MD simulations data of the sputtering yields and deposition rates, compare those with known experimental data, and discuss possible sources of discrepancy between simulation and experimental data.

Surface Science
Room 210C - Session SS+EM+SC-ThA

Compound Semiconductor Growth and Surface Structure

Moderator: A.R. Smith, Ohio University

2:00pm **SS+EM+SC-ThA1 III/V Semiconductor Surfaces during Metalorganic Vapor-phase Epitaxy***, **R.F. Hicks,*** University of California, Los Angeles **INVITED**

{Thin films made from compound semiconductors, such as indium phosphide, gallium arsenide and their alloys, have key applications in electronic and photonic devices. These single-crystal materials are fabricated by metalorganic vapor-phase epitaxy (MOVPE). In our laboratory, an ultra-high vacuum system has been connected to a state-of-the-art MOVPE reactor so that the semiconductor surfaces may be characterized in the growth environment. The atomic composition and structure of these materials has been determined by scanning tunneling microscopy, infrared spectroscopy, reflectance difference spectroscopy, x-ray photoelectron spectroscopy, and ab initio molecular cluster calculations. It has been found that indium phosphide and gallium arsenide exhibit very different surface structures under MOVPE process conditions. A disordered double-layer of As atoms with a few alkyl radicals are adsorbed on GaAs (001), while on InP (001), the surface is terminated with H atoms adsorbed on P dimers. This latter structure exhibits a single-domain (2x1) reconstruction. Another interesting example of III/V semiconductor surface chemistry is the formation of InGaAs/InP interfaces. Localized strain produces atomic arrangements that are distinct combinations of InP and InAs reconstructions. The application of this knowledge to the growth of epitaxial device structures will be discussed. @FootnoteText@ invited by David Castner.}

2:40pm **SS+EM+SC-ThA3 Quantitative Analysis of Indium Concentration in InGaAs Quantum Dots and Wetting Layers Using Cross-sectional Scanning Tunneling Microscopy***, N. Liu, S. Govindaraju, A.L. Holmes Jr.,* ***C.-K. Shih,*** University of Texas at Austin

Scanning tunneling microscopy has been employed to explore self-assembled InGaAs quantum dots (QDs) grown by migration enhanced epitaxy (MEE). With atomic resolution, compositional analysis has been done for both the QDs and wetting layers quantitatively. We found that both vertical and lateral segregation play important roles during the formation of the islands and thereafter capping procedure. Depletion of the wetting layer, due to the formation of the QDs, is demonstrated. More importantly, it is found that after capping the amount of existing indium in the QDs and WL is less than that of deposited indium, indicating a portion of deposited indium atoms was evaporated to the vacuum during overgrowth of GaAs. This observation is different from previous results, which proposed indium re-distribution within GaAs matrix after capping growth. Based on the observed data, a growth model is also proposed.

3:00pm **SS+EM+SC-ThA4 Surface Science of Gallium Nitride and Related Alloys***,* ***R.M. Feenstra,*** Carnegie Mellon University **INVITED**

The formation and structure of various faces of GaN, including adsorbed layers of Al, In, or H, are discussed. The primary preparation method is plasma-assisted molecular beam epitaxy although a comparison of results from metal-organic vapor phase epitaxy will also be presented. Experimental results from scanning tunneling microscopy allow us to broadly determine the characteristics of the surface structures, and first principles theory is then used to determine the precise atomic arrangements. For the case of surfaces grown by vapor phase epitaxy spectroscopic ellipsometry is used to identify the relevant surface phases. In contrast to other semiconductor surfaces, a central feature of many GaN reconstructions is their tendency to form metallic overlayers of metal (Ga, In, or Al) atoms. The terminating layers of metal atoms also leads to novel aspects of the surface kinetics - N atoms are predicted to diffuse easily between the metal layers, thus yielding enhanced surface diffusivity for those surfaces which are terminated by more than one layer of metal atoms. @FootnoteText@ Work performed with Y. Dong, C. D. Lee, H. Chen, A. R. Smith (CMU); J. E. Northrup (PARC); J. Neugebauer (FHI, Berlin); C. Cobet, T. Schmidtling, M. Drago, N. Wollschlaeger, N. Esser, W. Richter (TU, Berlin); and supported by NSF and ONR.

3:40pm **SS+EM+SC-ThA6 First Scanning Tunneling Microscopy and Spectroscopy Study of c-GaN(001)-4x1 Tetramer Structure and SIESTA Surface Simulation***,* ***H.A. Al-Brithen****, M.B. Haider, N. Sandler, A.R. Smith,* Ohio University*; P. Ordejon,* Institudo de Cienias de Materiales, Spain

Although early papers of the surface structure of c-GaN(001) reported 2x2 and c(2x2) reconstructions,[a] it was later shown both experimentally[b] and theoretically[c] that the intrinsic reconstruction is 4x1. However, until now, this 4x1 reconstruction has never been reportedly observed in real space. We have grown c-GaN on MgO(001) using radio frequency nitrogen plasma molecular beam epitaxy under Ga-rich conditions. RHEED patterns show that GaN(001) clearly exhibits 1x1 reconstruction during and after the growth; in fact, after cooling to ~ 200 °C a reversible disorder-order transition from 1x1 to 2x occurs, which may have been neglected or confused in earlier experiments with 2x2. This 2x is imaged using STM, finding that it is actually c(4x16) for Ga-rich growth and c(4x20) for more Ga-rich growth; STS spectra suggest that GaN(001)-c(4x16) is metallic. Annealing the film at T@sub s@ ~ 700-800 °C leads to the 4x1 reconstruction, as indicated by RHEED. STM performed on c-GaN(001)-4x1 shows that the surface consists of rows aligned along [110] with row spacing of 12.8 Å. Dual-bias STM images show a 180@super o@ phase shift of the filled and empty states profiles, as the sample bias changes from -1.2 V to +1.2 V, consistent with our recent simulated STM images, calculated using SIESTA code based on the tetramer model, showing that the filled state peak centered on the tetramer corresponds to the empty state minimum. STS acquired on the tetramer surface agrees with the semiconducting nature of 4x1, having a surface gap of 1.3 eV. In fact, the 4x1 tetramer structure was also predicted for c-AlN(001)[d], which widens the importance of understanding this reconstruction. Work is supported by NSF. @FootnoteText@ [a] Brandt et al., Phys. Rev. B R2253 (1995). [b] Feuillet et al., Appl. Phys. Lett. 70(8) (1997). [c] Neugebauer et al., Phys. Rev. Lett. 80(14) (1998). [d] Felice et al., Appl. Phys. Lett. 74(15) (1999).

4:00pm **SS+EM+SC-ThA7 Ion Induced Step Debunching of GaN***,* ***B. Cui,*** *P.I. Cohen,* University of Minnesota*; A.M. Dabira,* SVT Associates, Inc.

The development of surface morphology during ion bombardment has been described in terms of the curvature dependence of the sputtering yield [1] and asymmetric kinetics for the attachment of surface adatoms and vacancies at step edges [2]. We have used a Kaufman ion source to study the low energy ion effects during the MBE growth of GaN on sapphire substrates and GaN templates, comparing the results to these models. From a macroscopic point of view our measurements on GaN show quantitative agreement with the curvature driven theories. In particular we use the cross-over between Ga-limited growth and N-limited growth to estimate the N adatom concentration, a key ingredient of the theory. From a microscopic view, however, our RHEED and AFM studies have observed step debunching of multilayer steps and the elimination of hillock spirals. In these measurements, the starting GaN(0001) templates had 20 layer high mesas. After growth, round, nanoscale dimple structures, ranging from 90 nm to 850 nm, with bilayer steps were produced. This was seen with both Ar and nitrogen ions at energies ranging from 100-1200 eV. The size of the dimples and the terrace length of the debunched steps decrease with increasing sample temperature. After ion assisted growth, islands are found at the edges of the debunched steps. By tuning the ion energy and growth rate, uniform distributions of GaN nanoparticles, with means ranging from 50 nm to 200 nm, can be prepared. By combining ion induced step debunching and growth, step flow growth at the debunched steps is obtainable. Partially supported by the NSF and the AFOSR. @FootnoteText@ 1. R. M. Bradley and J. M. E. Harper, J. Vac. Sci. Technol. A 6, 2390 (1988). 2. J. Kim, D. G. Cahill, and R. S. Averback, Phys. Rev. B 67, 045404 (2003).

4:20pm **SS+EM+SC-ThA8 Thermal Desorption of Deuterium from GaN(0001): A Sensitive Probe of Surface Preparation***,* ***C.M. Byrd,*** *J.N. Russell, Jr.,* Naval Research Laboratory

Gallium nitride (GaN) is a wide band gap semiconductor with applications in high temperature, power and frequency optoelectronic devices. The surface chemistry of hydrogen on GaN affects growth rates and electronic passivation, while annealing temperatures impact both ohmic contacts and thermal stability. In this work, the preparation of a GaN(0001) thin film surface was investigated as a function of anneal temperature (300-1100K) using Auger electron spectroscopy (AES), electron energy loss spectroscopy (EELS), low energy electron diffraction (LEED), and temperature programmed desorption (TPD). After the GaN(0001) surface was sputter cleaned with nitrogen (N@sub 2@@super +@) ions, N@sub 2@ desorption was observed at 950 K from embedded nitrogen and then above 1200 K from GaN decomposition. EELS and AES showed subtle changes as the anneal temperature increased, and the LEED pattern sharpened. TPD spectra were collected for a series of anneal temperatures. After annealing the surface and cooling to room temperature, the surface was dosed with D atoms. When heated at 1 K/s, D@sub 2@ thermal desorption was observed, but not ammonia or gallane. There were four D@sub 2@ thermal desorption peaks at 430, 600, 730 and 810 K, the appearance and relative intensities of which were related to whether the anneal occurred at, above, or below the embedded nitrogen desorption temperature. Correlation of the anneal temperature dependence of the D@sub 2@ thermal desorption with the EELS, AES, and LEED data aided in identifying the origins of the D@sub 2@ desorption states. This work demonstrates D@sub 2@ thermal desorption is very sensitive to the quality of the GaN(0001), and explains differences in hydrogen on GaN(0001) TPD results in the literature.

4:40pm **SS+EM+SC-ThA9 Metal/Semiconductor Phase Transition in CrN Grown by Molecular Beam Epitaxy and Scanning Tunneling Microscopy**, ***C. Constantin***, *M.B. Haider, A.R. Smith,* Ohio University

Considerable interest has been of late in transition metal nitrides thin films/surfaces, which have both magnetic and electronic properties with potential applications in spintronics. CrN is a particularly interesting case, having a known correlation of structural and magnetic transition from a B@sub 1@ NaCl-paramagnetic to an orthorhombic-antiferromagnetic at T@sub Neel@=273-286K@footnote 1@. However,the reported electronic properties of CrN are controversial, and there has been no consensus whether the material is a metal or a semiconductor@footnote 2,3@. In this study, CrN is grown on MgO(001) at a substrate temperature of 450°C by a novel molecular beam epitaxy method for obtaining smooth surfaces. Bulk measurements reveal that the films are single crystal, and stoichiometric. The 1x1 face-centered cubic (fcc) surface structure is clearly distinguishable as obtained (for the first time) in room temperature atomic resolution scanning tunneling microscopy. In addition to the atomic resolution, long-range topographic distortions [LTD] are also seen on the surface, as also observed for the semiconductor ScN (001)@footnote 3@ and other nonpolar III-V surfaces. LTDs are characteristic of semiconductor surfaces, and are related to localized charge accumulation from impurities. Resistivity was measured from 77 to 450K; metallic behavior is found up to 260K (in contrast with some earlier reports) and semiconductor behavior above 285K. The bandgap obtained from resistivity data,71±0.315meV, agrees with the tunneling spectroscopy of the surface which show a very small gap. Consistent results have now emerged in which CrN has a semiconductor-metal phase transition corresponding to its magnetic transition. @FootnoteText@ @footnote 1@ A. Filippetti et.al, Phys. Rev. B 59, 7043 (1999)@footnote 2@J. D. Browne et.al, Phys. Status Solidi 1, 715 (1970)@footnote 3@P. S. Herle et.al, J. Solid State Chem. 134, 120 (1997)@footnote 4@H. A. Al-Brithen et.al, submitted to Phys. Rev. B.

Surface Science
Room 210B - Session SS1-ThA
Metal Oxides and Clusters IV: Oxide Surface Chemistry

Moderator: F. Zaera, University of California Riverside

2:00pm **SS1-ThA1 Partial Dissociation of Water on the Surface of ZnO**, ***B. Meyer***, *D. Marx,* Ruhr-Universität Bochum, Germany*; O. Dulub, U. Diebold,* Tulane University*; M. Kunat, D. Langenberg, C. Wöll,* Ruhr-Universität Bochum, Germany

Due to the interplay between chemical bonding, van der Waals forces, and hydrogen bonding, the interaction of water with solid substrates gives rise to complex phenomena such as complete dissociation, partial dissociation at defects, multilayer formation, and wetting. Recently, an intriguing, yet controversial, intermediate scenario was advanced, where the interaction between water molecules results in a partial dissociation of water on perfect surfaces, leading to superlattices with long-range order. Applying a broad array of methods, including diffraction (He-atom scattering, LEED), scanning tunneling microscopy, and thermodynamic measurements supplemented by density-functional total-energy, Car-Parrinello molecular dynamics, and STM computations, conclusive evidence is given that such a phenomenon is encountered for H@sub 2@O on the perfect ZnO(10-10) surface. At monolayer coverage, every second water molecule is found to auto-dissociate, subject to a low activation barrier, upon a favorable hydrogen-bonding interaction with a neighboring water molecule, i.e. without the need to invoke defects or impurities. This process leads to a (2x1) superlattice with long-range order which is stable from well below room temperature up to temperatures close to the boiling point of liquid water.

2:20pm **SS1-ThA2 Photoemission of Adsorbed Xenon Studies on the Characterization of Reaction Sites on Oxygen-Modified Ni(110) Surfaces**, ***H. Guo***, *F. Zaera,* University of California at Riverside

Considerable attention has been paid in our laboratory to the study of the adsorption and reactions of surface intermediates of relevance to catalysis on clean, hydrogen- and oxygen-modified Ni(110) to understand the properties of these surfaces in hydrocarbon conversion, and in trying to identify specific sites selective for the promotion of desirable reactions. STM studies have evidenced that surface oxygen in lower coverage regimes not only induces reconstruction of Ni(110) in extending domains, but also modifies the electronic structure at local sites. Such surfaces have been found particularly effective in the production of heavier hydrocarbons. However, the relationship between this distinctive catalysis and the surface structures responsible for it cannot be established without a better knowledge of the local surface properties at the atomic scale. With this in mind, we have carried out experiments using photoemission of adsorbed xenon (PAX) to characterize specific adsorption sites in heterogeneous surfaces produced by oxygen adsorption on Ni(110) single crystals. This technique, which provides both energetic and local electronic information on small surface atom ensembles, has been used in combination with chemical titrations using probe molecules such as carbon monoxide and ammonia to determine correlations between electronic structures and reactivity. It was determined that ammonia prefers a direct interaction with the terminating atoms of the -Ni-O- added rows that form on Ni(110) upon oxygen treatments. Those sites appear to be key for the selective conversion of hydrocarbons.

2:40pm **SS1-ThA3 Oxide and Carbonate Surfaces as Environmental Interfaces: The Importance of Water in Surface Composition and Surface Reactivity**, ***V.H. Grassian***, University of Iowa **INVITED**

Environmental molecular surface science is an important and expanding area of current research. This presentation focuses on advances in the molecular level understanding of the chemistry that occurs on oxide and carbonate surfaces in the atmosphere. In particular, the importance of water in the surface composition and surface reactivity of two representative oxide and carbonate surfaces, MgO(100) and CaCO@sub3@(104) will be discussed. Reactions of trace atmospheric gases, including HNO@sub3@, with MgO(100) and CaCO@sub3@(104) as a function of relative humidity highlight the role of surface hydroxyl groups and molecularly adsorbed water in these reactions.

3:20pm **SS1-ThA5 Interactions of S-containing Molecules and Water Vapor with Polycrystalline UO@sub 2@**, ***B.V. Yakshinskiy***, *T.W. Schlereth, M.N. Hedhili, T.E. Madey,* Rutgers, The State University of New Jersey

The interaction of sulfur dioxide (SO@sub 2@), thiophene (C@sub 4@H@sub 4@S) and water vapor (D@sub 2@O) with a polycrystalline stoichiometric UO@sub 2@ and oxygen-deficient UO@sub 2@ surfaces has been studied under UHV conditions over the temperature range 100 K to 600 K, using XPS (X-ray photoelectron spectroscopy) and TPD (temperature programmed desorption). This work is motivated by potential catalytic applications of stockpiles of depleted uranium. All three molecules are relatively unreactive on the stoichiometric UO@sub 2@ surface, they adsorb and desorb in molecular form. The creation of oxygen vacancies by 1.5 keV Ar ion sputtering is found to enhance the UO@sub 2@ surface reactivity towards the desulfurization of C@sub 4@H@sub 4@S and SO@sub 2@ and the dissociation of water with formation of OD species. Heating of the oxygen-deficient surface with a preadsorbed water monolayer causes desorption of molecular D@sub 2@. The oxygen remains and restores the sample surface to its initial stoichiometric state. The healing of sub-surface defects occurs through thermal diffusion of atoms from the sample bulk at ~ 500 K.

3:40pm **SS1-ThA6 Reactions of Substituted Hydrocarbons with Cerium Oxide Thin Films@footnote1@**, ***D.R. Mullins***, *M.D. Robbins, T.S. McDonald,* Oak Ridge National Laboratory

Fully oxidized ceria surfaces are largely inactive with respect to the adsorption and reaction of most adsorbates under UHV conditions. Reduced surfaces, however, provide active sites where some adsorbates such as H@sub 2@O, NO and SO@sub 2@ can adsorb and react. Other molecules, such as CO, H@sub 2@ and C@sub 2@H@sub 4@ do not interact strongly with either an oxidized or a reduced surface. Based on the ethylene behavior, it appears that hydrocarbons may not interact strongly with ceria whereas on metals they frequently decompose. Substituted hydrocarbons may therefore bind to the surface through the heteroatom at the oxygen vacancy while the hydrocarbon part of the molecule may not interact strongly with the surface. We have recently completed a study of methanol and methanethiol adsorption on ceria as a function of temperature, exposure and Ce oxidation state. CH@sub 3@OH reacts at low temperatures with oxidized CeO@sub 2@ to produce H@sub 2@O at 200 K, and CH@sub 2@O and CH@sub 3@OH near 600 K. This leads to the reduction of the ceria. This is the first molecule we have examined that is capable of reducing a ceria film in UHV. Surprisingly, CH@sub 3@SH does not interact strongly with the CeO@sub 2@. It desorbs molecularly by 300 K and does not reduce the oxidized surface. On reduced ceria, the oxygen vacancies result in more methanol adsorption which undergoes more extensive decomposition producing CO and H@sub 2@ near 600 K. As the degree of ceria reduction increases, more H@sub 2@ and less H@sub 2@O are produced. Methanethiol does adsorb on the reduced surface producing CH@sub 3@S and OH. The C-S bond cleaves near 600 K and methyl reacts with the hydroxyls to produce CH@sub 4@. @FootnoteText@ @footnote 1@ Research sponsored by the Division of Chemical Sciences, Geosciences, and Biosciences, Office of Basic Energy Sciences, U.S. Department of Energy, under contract DE-AC05-00OR22725 with Oak Ridge National Laboratory, managed and operated by UT-Battelle, LLC.

4:00pm **SS1-ThA7 Adsorption and Reaction of Acetaldehyde and Methanol on Stoichiometric and Defective Mixed-Metal Oxide Surfaces**, ***L.Q. Wang**, S.A. Azad, K.F. Ferris, C.H.F. Peden, M.H. Engelhard,* Pacific Northwest National Laboratory

The adsorption and reaction of oxygenated hydrocarbons on metal oxide surfaces are of much interest from both fundamental and practical perspectives. The reactivity of these catalytic processes largely depends on the characteristics of the oxide catalysts defined by their surface structures, acid-base properties and surface defects. Oxygenated hydrocarbons are often used as fuels and fuel additives , and they may be formed as a result of incomplete combustion of fuel in the engine. To efficiently reduce these toxic exhaust products, it is especially helpful to have a fundamental understanding of the adsorption and reaction of oxygenated hydrocarbons on metal oxide surfaces. In this presentation, we examined the interactions of acetaldehyde and methanol with stoichiometric and defective SrTiO@sub 3@(100) surfaces using x-ray photoelectron spectroscopy (XPS), temperature programmed desorption (TPD), and first-principles density-functional calculations. The results obtained from methanol and acetaldehyde on SrTiO@sub 3@(100) surfaces are compared with our results on Ce@sub 0.8@Zr@sub 0.2@O@sub 2@(111) surfaces and with the previous results on single crystal TiO@sub 2@ surfaces. Both acetaldehyde and methanol adsorb mostly non-dissociatively on the stoichiometric SrTiO@sub 3@(100) surface that contains predominately Ti@super 4+@ cations. Theoretical calculations predict weak adsorption of acetaldehyde and methanol on TiO@sub 2@-terminated SrTiO@sub 3@(100) surfaces, in agreement with the experimental results. The stronger binding of acetaldehyde and methanol on TiO@sub 2@ surfaces than on SrTiO@sub 3@(100) surfaces is attributed to the more covalent nature of the Ti@super 4@@super +@ cation sites in the mixed-metal oxides and the unique surface structure due to the absence of the bridging oxygen atoms on the TiO@sub 2@-terminated SrTiO@sub 3@(100). The Ti@super 4@@super +@ sites on the stoichiometric SrTiO@sub 3@(100) surface are not sufficiently active for surface reactions such as aldol condensation, as opposed to the Ti@super 4@@super +@ ions on the TiO@sub 2@ (001) surface. However, decomposition and redox reactions for both methanol and acetaldehyde occur in the presence of surface defects created by Ar@super +@ sputtering. The decomposition products following reactions of acetaldehyde on the defective surface include H@sub 2@, C@sub 2@H@sub 4@, CO, C@sub 4@H@sub 6@ and C@sub 4@H@sub 8@. Reductive coupling to produce C@sub 2@H@sub 4@ and C@sub 4@H@sub 8@ is the main reaction pathway for decomposition of acetaldehyde on the sputter reduced SrTiO@sub 3@(100) surface. Adsorption of CH@sub 3@OH on the reduced SrTiO@sub 3@(100) surface produces the decomposition products of H@sub 2@, CO, and CH@sub 4@. As compared with SrTiO@sub 3@(100) surfaces, Ce@sub 0.8@Zr@sub 0.2@O@sub 2@(111) surfaces exhibit enhanced adsorption and reactivity for methanol and acetaldehyde. Both acetaldehyde and methanol mostly adsorb dissociatively on the oxidized Ce@sub 0.8@Zr@sub 0.2@O@sub 2@(111) surfaces. The formation of furan was surprisingly observed on reduced Ce@sub 0.8@Zr@sub 0.2@O@sub 2@(111) surfaces following the adsorption of acetaldehyde.

4:20pm **SS1-ThA8 The Adsorption of Bromobenzene on Periodically-Stepped and Flat NiO(100) Surfaces**, ***S.C. Petitto**, E.M. Malone, M.A. Langell,* University of Nebraska-Lincoln

Bromobenzene was adsorbed onto both stepped and flat NiO(100) surfaces to model surface defects relevant to heterogeneous chemical processes. Both surfaces were characterized using Auger electron (AES) and X-ray photoelectron (XPS) spectroscopies, low energy electron diffraction (LEED), and thermal desorption mass spectrometry (TDS). The stepped NiO(100) substrate was cut and polished at an angle vicinal to the (100) surface, resulting in monoatomic steps with 7-atom terraces. The LEED diffraction patterns show sharp diffraction features for both surfaces, and diffraction spot splitting correlating to appropriate terrace and step height dimensions for the stepped surface. Both substrates interact with bromobenzene at 120 K to produce first a molecularly adsorbed monolayer species and then a multilayer adsorbate state as the exposure is increased. The stepped NiO(100) surface has an additional TDS peak not observed for flat NiO(100) and which results in dissociation adsorption initiated by cleavage of the Br-C@sub 6@H@sub5@ bond. Bromine that remained on the surface appeared as nickel bromide.

4:40pm **SS1-ThA9 Synchrotron X-Ray Photoelectron Spectroscopy Studies of the Thermal Chemistry of (trimethyl) Methylcyclopentadienyl Platinum on Tio@sub 2@ (110)**, ***K. Adib**,* Brookhaven National Laboratory; *M.A. Barteau,* University of Delaware; *J. Hrbek,* Brookhaven National Laboratory; *J.M. White,* University of Texas at Austin

Pt/TiO@sub 2@ is one of the most important systems used in the photocatalytic decomposition of water to hydrogen as well as environmental purification of organic waste. In this regard, the use of organometallic precursors as sources of Pt metal islands on TiO@sub 2@ surfaces offers an attractive alternative to metal-vapor deposition techniques. We have used synchrotron X-ray photoelectron spectroscopy (XPS) to investigate the thermal chemistry of (trimethyl) methylcyclopentadienyl platinum (MeCpPtMe@sub 3@) on the stoichiometric rutile (110) surfaces. Our results indicate that the submonolayer adsorption of MeCpPtMe@sub 3@ on nominally stoichiometric TiO@sub 2@ (110) at 300 K does not result in substantial decomposition of the adsorbate. While subsequent annealing of the surface to 450 K enhances the decomposition of the MeCpPtMe@sub 3@, as evidenced by the appearance of additional Pt 4f peaks, there is no evidence of the desorption of the resulting carbon fragments even after extended periods of annealing. Predosing of nominally stoichiometric TiO@sub 2@ (110) surfaces with molecular oxygen at 300 K substantially enhances the decomposition of subsequently deposited MeCpPtMe@sub 3@. This decomposition is accompanied by the formation surface-bound CO@sub x@ species, possibly carboxylate groups, suggesting strong interactions between the adsorbate and substrate. Heating to 850 K can result in the removal of more than 98% of the surface bound carbon species, including the CO@sub x@, but does not result in the formation of a carbon-free Pt/TiO@sub 2@ surface.

5:00pm **SS1-ThA10 The Reaction of DL-Proline on TiO@sub2@(110) Single Crystal Surfaces.**, *K. Adib,* Brookhaven National Laboratory; *G. Fleming,* University of Auckland, New Zealand; *J.A. Rodriguez,* Brookhaven National Laboratory; ***H. Idriss**,* University of Auckland, New Zealand; *M.A. Barteau,* University of Delaware

Titanium metal is widely used as a medical implant in the aiding of healing fractures in teeth and bone. The choice of titanium as an implant material is based on both its mechanical properties and on its relative chemical inertness. Once placed in the body's aqueous environment, the implant undergoes an oxidation process where the formation of a thin oxide layer in the range of 10 to 100 nm thick occurs. This layer is crucial since it prevents the Ti metal from further reacting with the biological molecules. However, the nature of interaction of the bio-molecule with this thin TiO@sub2@ surface will ultimately determines its conformation. If the conformation of the bio-molecule is altered from its naturally occurring state, it may cause the body to undergo an auto immune response and reject the implant. Surface science studies can address the nature of interaction of prototype amino acids with TiO@sub2@. In this work we study the reaction of DL-Proline on the surface of a model TiO@sub2@ surface, the rutile (110) surface. Proline was chosen as it is a constituent of collagen I, a major high tensile structural protein found in teeth, bone and cartilage. The reaction of DL-Proline on stoichiometric and O-defected surfaces has been investigated by temperature programmed desorption while the surface species at different reaction temperatures were monitored by X-ray core level shifts and by their valence band. Proline binds to the surface via its COO group. The presence of two N(1s) lines upon adsorption at 300 K indicates the presence of two distinct species that are tentatively assigned to -NH@sub2@@super+@- and -NH- attributed to the zwitterionic and non-zwitterionic forms of the amino acid, respectively. Complex reactions are seen for Proline upon heating the surface, and products such as CH@sub2@=C=O and HCN are seen in the gas phase. In addition, large amounts of organic species containing O and N are still present on the surface even after heating to 600 K.

Surface Science
Room 213B - Session SS3-ThA
Surface Diffusion and Transport

Moderator: L. Bartels, University of California, Riverside

2:00pm **SS3-ThA1 Molecular Transport on the Nano-Second Timescale; Co/cu(001).***, **G. Alexandrowicz**[1],* University of Cambridge, UK*; A.P. Jardine,* University of Cambridge, UK, U.K.*; H. Hedgeland,* University of Cambridge, UK*; P. Fouquet,* Institut Laue-Langevin, France*; S. Dworski, W. Allison, J. Ellis,* University of Cambridge, UK

The measurement of surface diffusion on microscopic length scales presents a considerable experimental challenge. Measurements are typically restricted to specific systems which either diffuse sufficiently slowly for real time techniques, such as STM, to be applied or fast enough to be seen using Quasielastic Helium Atom Scattering (QHAS). Here, we present the first surface diffusion measurements from the unique new Cambridge @super 3@He Spin Echo Spectrometer@footnote 1@@footnote 2@. The apparatus makes use of the @super 3@He Spin Echo technique@footnote 3@ to improve upon existing QHAS resolution by three orders of magnitude, showing new insights into previously inaccessible experimental regimes. We have studied the prototypical molecular system; CO/Cu(100). Existing QHAS measurements on this system were very limited@footnote 4@ and the intense debate over the difference between potential energy surfaces extracted from the measurements and from first principle calculations@footnote 5@ was left unresolved. Our measurements show the system is diffusing well within the previously unmeasurable regime. Quasielastic broadenings were measured as function of momentum transfer and temperature and interpreted using MD simulations. The analysis reveals a Potential Energy Surface, illustrating the success and limitations of recent first principle calculations@footnote 6@, and serves as a bench mark for further theoretical improvements. @FootnoteText@ @footnote1@ AP Jardine, P Fouquet , S Dworski, G Alexandrowicz, J Ellis, W Allison, To be published @footnote2@ S Dworski, G Alexandrowicz, P Fouquet, AP Jardine, W Allison, J Ellis. Rev. Sci. Inst. In press. 2004. @footnote3@ C Shmidt, D Scholz, U Spinola, M Dekivit, D Dubbers. Phys. Rev. Lett. 75(10):1919-1922 @footnote4@ AP Graham, JP Toennies, Surf. Sci. 427-428 (1999) @footnote5@ Q G, DA King, J. Chem. Phys. 114(2001) 1053 @footnote6@ P Fouquet, RA Olsen, EJ Baerends, J. Chem. Phys. 119(2003) 509-514.

2:20pm **SS3-ThA2 CO Diffusion on Cu(111): Effects of CO-CO Interactions***, **B.V. Rao**, R. Perry, A. Liu, L. Bartels,* University of California, Riverside

Diffusion is the surfaces process that occurs most frequently and, thus, may arguably be regarded the most important one. With the advent of low-temperature scanning tunneling microscopy one is able to image and track the motion of individual atoms and molecules on surfaces for long periods of time@footnote 1@. We probed the diffusion of CO molecules on Cu(111) at temperatures between 17 and 50 K. At 17K, molecular hops are infrequent and occur on the time-scale of hours, whereas at 50K the hopping frequency has reached >1 Hz. Measurements at various temperatures indicate that the diffusion of isolated CO molecules follows an Arrhenius behavior. Our investigation puts special attention on the effect of neighboring CO molecules on the hopping direction and frequency. Preliminary results suggest, that the CO-CO interaction enhances or decreases CO diffusion depending on the separation of the molecules. The distance dependence resembles the oscillation patter of the Cu(111) surface state, similar to Cu adatom interactions previously reported by Repp et al.@footnote 2@. @FootnoteText@ @footnote 1@Briner, B.G., Doering, M., Rust, H.-P., Bradshaw, A. M., Science 278 (1997) 257.@footnote 2@Repp J., Moresco F., Meyer G., Rieder K.H., Hyldgaard P., Persson M., Phys. Rev. Lett., 85 (2000) 2981 .

2:40pm **SS3-ThA3 How Trace Amounts of S Enhances Self-Diffusion on Cu(111)***, W.L. Ling, **K.F. McCarty**, J. De la Figuera, K. Pohl, N.C. Bartelt,* Sandia National Laboratories

We find that <0.01 monolayer (ML) of S enhances surface diffusion on Cu(111) by several orders of magnitude. Using low-energy electron microscopy (LEEM) and scanning tunneling microscopy (STM), we probe the mechanisms of this enhancement by monitoring the decay rate of island stacks and the ripening of 2D island arrays as a function of S coverage and temperature. The decay rate of islands in stacks increases roughly as the S coverage cubed, consistent with the proposal that the enhanced surface diffusion is due to the formation of Cu@sub 3@S@sub 3@ clusters@footnote 1@. However, we also find a dramatic change in the mechanism of island-stack decay and the ripening of 2D island arrays as a function of S coverage. While island decay on clean Cu is diffusion limited@footnote 2@, this is not the case in the presence of a small amount of S. However, at higher S coverages, the kinetics revert to diffusion limited. Similarly, how island arrays evolve is strongly influenced by the S coverage. For clean Cu and at high S coverages, large islands grow at the expense of nearby small islands. In contrast, local ripening does not occur with smaller amounts of S -- mass flows from islands to the steps bounding large terraces. We show that the strong dependence of the surface kinetics on S coverage can be quantitatively understood if the Cu diffusion at low S coverages is limited by the rate of reaction of S and Cu to form Cu@sub 3@S@sub 3@ clusters. 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. @FootnoteText@ @footnote 1@P.J. Feibelman, Phys. Rev. Lett. 85, p. 606 (2000).@footnote 2@M. Giesen & H. Ibach, Surf. Science 431, p. 109, (1999) .

3:00pm **SS3-ThA4 Diffusion of Ir and W Atoms on W(110) @super *@***, **G. Antczak**, G. Ehrlich,* University of Illinois at Urbana-Champaign

Using field ion microscopy we have carried out extensive measurements of the migration of Ir and W atoms on the W(110) plane at temperatures from 300 to 370 K. In addition to nearest-neighbor jumps in the direction, we recognized three types of long jumps, which may contribute to diffusion: double jumps along , vertical jumps in the direction and the horizontal jumps in the direction. From analysis of the distribution of displacements, constructed from at least 1200 observations, we have found that long jumps play a significant role in diffusion at temperature higher than 340 K. The temperature dependence of all types of jumps was measured to derive activation energies and prefactors for diffusivities. Long jumps proceed with a higher activation energy and a higher prefactor than do single jumps for tungsten as well as for iridium atoms. The rate of single jumps is diminished by contributions from long jumps. However, contrary to expectation, the presence of long jumps does not raise the prefactor for diffusivity above the usual value. Comparisons are made of Ir with W and simple models accounting for our finding are proposed. @super *@Supported by the Department of Energy under Grant No. DEFG02-96ER45439 to the Materials Research Lab., and by the Petroleum Research Fund, under Grant ACS PRF No. 36919-AC5.

3:20pm **SS3-ThA5 Temperature-Dependent Thresholds for Ion-Stimulated Surface Diffusion: A Comparison of Si and Ge Substrates***, Z. Wang, **E.G. Seebauer**,* University of Illinois at Urbana-Illinois

Ion-surface interactions at low energies (<100 eV) characterize an increasingly diverse array of material processing steps in ion beam assisted deposition (IBAD), plasma enhanced deposition, reactive ion etching (RIE), and other applications. The governing kinetic phenomena are often tacitly considered to lie at one of two poles: physical effects where momentum matching dominates, and chemical effects involving thermal activation of atomic bonds according to Arrhenius expressions. Here we report surface diffusion measurements demonstrating behavior that lies at neither pole. Optical second harmonic microscopy is used to image diffusion of indium adsorbed on Si(111) and Ge(111) under low-energy noble-gas ion bombardment. Both systems exhibit a surprising tradeoff between substrate temperature and the energy threshold at which ion influences become manifest. Molecular dynamics simulations suggest that the effect originates from changes in surface point defect concentrations. Instantaneous nonuniformities in net surface potential induced by thermal vibrations provide a mechanism by which ions can affect these concentrations nonlinearly. The effects generally increase the rate of mass transport across the surface. The simulations and experiments agree in finding that an important factor determining the magnitude of the tradeoff is the strength of the adsorbate-substrate bond, which is lower for In/Ge than for In/Si.

3:40pm **SS3-ThA6 LEEM Observation of Island Decay on Si(110)***, **F. Watanabe**, S. Kodambaka, W. Swiech, G.D. Cahill,* University of Illinois at Urbana-Champaign

Laser texturing enables the observation of island decays on (1x1) high temperature phase of Si(110) surface in low energy electron microscopy by artificially creating large flat terraces. At temperatures above the phase transition (T = 790 ~ 980 Â°C), the decay of the island areas exhibits a nonlinear dependence on time, indicating the rate limiting process is surface diffusion. The aspect ratios of the islands during the decay show a weak temperature dependence. Following a methodology developed previously@footnote 1@, we have obtained kinetic parameters involved in

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

the island decay. The activation energy of mass transport and the free energy of kink formation have been determined to be 1.67 Â± 0.15 eV and 0.22 Â± 0.03 eV respectively. Based on this value for the kink energy and the equilibrium island shapes, we derive the angular dependence of the step energy and the step stiffness. @FootnoteText@ @footnote 1@ S. Kodambaka, V. Petrova, S. V. Khare, D. D. Johnson, I. Petrov, and J. E. Greene, Surf. Sci. 513, 468 (2002).

4:00pm **SS3-ThA7 Effects of Si Deposition on Electromigration Induced Step Bunching on Si(111)*, B.J. Gibbons,*** The Ohio State University*; J. Noffsinger,* The University of Kansas*; J.P. Pelz, C. Ebner,* The Ohio State University

We have studied the effects of Si deposition on direct current (DC) heating induced step bunching on Si(111) using Si samples with spherical dimples ground into the surface to create a range of surface miscut. With no Si deposition, we observe the well-known behavior that only "step-down" current produces bunching in temperature "Regime I": (<950°C), while bunching in "Regime II": (1050°C-1250°C) only occurs for "step-up" current. But in contrast to a report by Métois et al. [Surf. Sci. 440 (1999) 407] we very clearly do not observe that net growth conditions reverses the current direction required for bunching in Regime II. This is not consistent with the proposal [S. Stoyanov, Surf. Sci. 416 (1998) 200] that the primary bunching mechanism in Regime II is due to increased step permeability. However we do observe that there is a strong reduction in the density of "crossing steps" close to zero net deposition/sublimation conditions, qualitatively consistent with the simultaneous bunching/debunching model of Kandel and Weeks [Phys. Rev. Lett. 74 (1995) 3632]. We will discuss on-going work to quantify this reduction and compare it with 1D analytic and 2D Monte Carlo models. By measuring areas of the dimpled samples with different miscut, we have also found that the average step bunch height increases roughly linearly with sample miscut, but does not depend significantly on Si deposition conditions. We are also comparing this observed bunch-height dependence on miscut with 1D and 2D models to evaluate which existing model can best explain a range of step-bunching behavior. Work supported by NSF Grant DMR-0074416.

4:20pm **SS3-ThA8 Pb/Si(111) Domain Boundary Fluctuations*, D.B. Dougherty,*** University of Maryland at College Park*; W.G. Cullen, E.D. Williams,* MRSEC

The techniques of fluctuation statistics are applied to a common 1D interface on solid surfaces: a domain boundary between two surface phases. We describe variable temperature STM observations of fluctuating boundaries between Si(111)-(1x1)-Pb and Si(111)-@sr@3x@sr@3R30-Pb@footnote 1@. We establish the dominant mass transport mechanism for the fluctuations from the power-law growth in time of the temporal correlation function with an exponent of about 0.5. This behavior implies that fluctuations of the (1x1) boundaries occur via exchange of mass with a 2D adatom gas on the @sr@3x@sr@3 phase. This conclusion is corroborated by the extraction of the persistence probability from the same data, giving a persistence exponent of 0.75. This 2D exchange mechanism allows comparison of the nanoscale fluctuation kinetics with previous macroscopic surface science measurements. The 2D adatom gas has long been established for this system from the observation of zeroth-order desorption kinetics. Previous studies indicate a barrier for this rate-limiting exchange step of 2.3 eV@footnote 2@. Our experimental correlation functions yield an effective activation barrier of about 1.6 eV. This provides a direct physical confirmation of the indirect deduction of 2D exchange of mass at the domain boundary. Finally, the autocorrelation function of the boundary fluctuations can also be determined and used to extract correlation lengths that compare well with the size of (1x1) domains. In addition, these lengths are compared with correlation lengths for fluctuating steps on clean metal surfaces. *Supported by UMD-NSF-MRSEC under DMR-00-80008. @FootnoteText@ @footnote 1@ J. Slezak et al., Surf. Sci. 454 (2000) 584; O. Custance et al., Surf. Sci. 482 (2001) 878.@footnote 2@ M. Saitoh et al., Surf. Sci. 154 (1985) 394.

4:40pm **SS3-ThA9 Temperature-Dependence of Submonolayer Island Structure and Multilayer Growth Morphologies in Ag/Ag(111) Homoepitaxy*, M. Li,*** *E. Cox, C. Chung, C. Ghosh, J. Evans, P.A. Thiel,* Iowa State University

We have performed STM studies to analyze the irregular structure of submonolayer islands and the rough wedding-cake-like multilayer growth morphologies formed during Ag/Ag(111) homoepitaxy between 120-180K. Previous STM and surface scattering studies have probed only selected aspects of these features of film structure, which are expected due to restricted periphery diffusion (PD) and limited interlayer transport. However, no comprehensive real-space characterization of film morphology across this temperature regime has been available. KMC simulation of atomistic lattice-gas models is also viable in this regime where island separations are below ~100nm, and film morphology is not controlled by dislocations (in contrast to behavior at 300K). We have thus also developed a realistic atomistic model to describe the submonolayer growth of individual islands, and thereby quantified the observed transition with increasing temperature from dendritic shapes with triangular envelopes (due to anisotropy in incorporation at corners) to more isotropic fractal shapes (reflecting high edge and kink rounding barriers), and then to compact shapes (reflecting efficient PD). More complete modeling of the overall island nucleation and growth process revealed a transition to reversible island nucleation in this temperature range. Finally, by extending of our realistic model for submonolayer island formation to the multilayer regime incorporating negligible interlayer transport, we described quantitatively the observed kinetic roughening and wedding-cake-like growth morphologies.

Thin Films
Room 303C - Session TF-ThA
Photovoltaic Thin Films

Moderator: T. Klein, The University of Alabama

2:00pm **TF-ThA1 Study of Molybdenum Back Contact Layer to Achieve Adherent and Efficient CIGS2 Absorber Thin-Film Solar Cells***, N.G. Dhere,* Florida Solar Energy Center*; **A.A. Kadam,*** University of Central Florida

Molybdenum is used as back contact layer in CuIn@sub 1-x@Ga@sub x@S2 (CIGS2) absorber thin film solar cells. Mo is sputter deposited using DC magnetron sputtering. Mo being refractory material develops stresses. It is essential to deposit stress-free and relatively inert Mo in order to achieve well adherent and highly efficient CIGS2 absorber thin film solar cells on stainless steel and glass substrates. Earlier studies have shown that films deposited at 300 W and 0.3 mT pressure develops compressive stress, while the films deposited at 200 W and 5 mT pressure develops tensile stress. Four experiments were carried out to achieve optimum deposition cycle to deposit stress free Mo. In first experiment two cycles of 200 W/5 mT were sandwiched between three cycles of 300 W/0.3 mT. In second experiment two cycles of compressive stress were sandwiched between three cycles of tensile stress. In third experiment two cycles each of compressive stress and tensile stress were deposited alternatively starting with compressive cycle and ending with tensile cycle. The fourth experiment was conducted in reverse order, starting with tensile and ending with compressive. All the depositions were carried out on 15 x 10 cm@super 2@ stainless steel substrates. 5 x 10 cm@super 2@ strip was cut and remaining 10 x 10 cm@super 2@ was deposited with metallic precursors copper-gallium and indium. Metallic precursors were sulfurized at 475°C for 20 minutes in a gas mixture of 4% H@sub 2@S/N@sub 2@. The presentation describes the XRD and SEM analysis to study the quality of films as a consequence of deposition cycle of Mo back contact layer. TEM analyses are also presented to study Mo/CIGS2 interface behavior. Small region of Mo films on remaining 5 x 10 cm@super 2@ strips were tested for adhesion by simple scotch tape test and remaining part was sulfurized at 475°C for 20 minutes to study the reactivity of Mo with H@sub 2@S at the operating temperature.

2:20pm **TF-ThA2 Formation of Chalcogen Containing Plasmas and Their Use in Synthesis of Photovoltaic Absorber Layers*, S. Kosaraju,*** Colorado School of Mines*; C.A. Wolden,* Colorado school of Mines*; R. Ingrid,* ITN Energy Systems, Inc.

The synthesis of copper chalcopyrite solar absorbers requires high temperature and excess chalcogen due to low chalcogen reactivity. This paper describes work aimed at addressing these issues through plasma processing. An inductively coupled plasma (ICP) source was used to activate both sulfur and selenium vapors into high-energy atomic and radical species. Stable ICP discharges were achieved with both sulfur and selenium vapors using argon as a carrier gas. ICP processing configurations are described for both a flowtube geometry used for metal selenization as well as for incorporation into a high vacuum co-evaporation environment. Actinometry was employed to measure the flux of chalcogen vapors from solid sources as a function of source temperature and the RF power. The potential of this approach was demonstrated by converting indium and copper/indium/gallium films to chalcopyrites using the ICP source. It is shown that indium is readily converted to In@sub 2@Se@sub 3@ using argon/selenium plasma at room temperature. Similarly, Cu/In/Ga precursor thin films on a stainless steel substrate were exposed to plasma-activated selenium at 300@super o@C. The foils were converted into ternary and quandary chalcopyrite compounds, and no crystalline binary phases (i.e. In@sub 2@Se@sub 3@, CuSe) were observed. Films were additionally characterized by scanning electron microscopy and energy dispersive spectroscopy.

2:40pm **TF-ThA3 Thin Film Photovoltaics***, **N.G. Dhere**,* Florida Solar Energy Center **INVITED**

The world production of photovoltaic (PV) cells/modules has increased at a rate of >35%/year from 88.6 MW in 1996 to 744.8 MW in 2003 with concomitant reduction in cost. During this period U.S. fraction of PV production has dropped from 44% to 14%. Last year, U.S. production of thin-film PV modules was as follows: CdTe First Solar 2.5 MW, CuIn@sub 1-x@Ga@sub x@Se@sub 2-y@S@sub y@ (CIGS) Shell Solar 2 MW, a-Si:H UniSolar 7 MW and CIGS Global Solar 0.5 MW. Because of considerable increase in the production capacity, it is expected that the cumulative U.S. production of thin-film PV modules will double to 25 MW this year and again to 50 MW next year, thus spearheading production growth. Present PV conversion efficiencies of champion thin-film solar cells are CIGS 19.3%, CdTe 16.5% and a-Si:H 12.4%. However, those of PV modules lag considerably behind. In addition to increasing efficiency and production volume of thin-film PV modules and reducing their cost, it is also important to assure their long-term reliability. Other principle research issues in thin-film photovoltaics are discussed below. Even though the bandgaps of CdTe and CuIn@sub 1-x@Ga@sub x@S@sub 2@ (CIGS2) are near optimum for terrestrial and space applications, their open circuit voltages are considerably below theoretical attainable values. Therefore, interdiffusion, phase formation, and accumulation of impurities in the active junction region must be studied. Moreover, as CIGS film transitions from Cu-rich to In-rich composition, its microstructure must be studied. Obtaining ohmic contacts is difficult especially for CdTe because of the inherently low p-type doping level. Therefore, increasing p-type doping level is important. FSEC PV Materials Lab is participating in this effort with research and development on large area CIGS thin-film solar cells as well as by leading in testing of U.S. thin-film PV modules in the hot and humid environment as well as under high-voltage bias conditions.

3:20pm **TF-ThA5 Reaction Kinetics of Cu with the CdTe(111)-B Surface***, **G. Teeter**, C.L. Perkins, T. Gessert,* National Renewable Energy Laboratory*; C. Corwine,* Colorado State University*; S. Asher,* National Renewable Energy Laboratory

Copper is frequently incorporated at the back contacts of CdTe-based thin film photovoltaic devices, where it is believed to dope the CdTe p-type and aid in the formation of a pseudo-ohmic contact. In the present study, the reaction kinetics of Cu thin films (0-30 Å) with the CdTe(111)-B surface have been measured via mass spectrometry in ultrahigh vacuum. Cu was deposited on the clean surface, and upon annealing it was observed that atomic Cd desorbs from the surface in proportion to the amount of deposited Cu. Temperature programmed desorption (TPD) measurements reveal zero order reaction kinetics for the Cu/CdTe(111)-B system. In addition, surface composition maps generated by scanning Auger Electron Spectroscopy (AES) show that a metastable copper telluride phase forms at the surface under certain conditions.

3:40pm **TF-ThA6 Transparent and Semi-Transparent Conducting Film Deposition by Reactive-Environment, Hollow Cathode Sputtering***, A.E. Delahoy, **S.Y. Guo**,* Energy Photovoltaics, Inc.

Highly transparent and conductive In@sub 2@O@sub 3@ and ZnO films containing different doping elements such as Mo, Zr, Nb, Ta, W (for In@sub 2@O@sub 3@) and Al, B (for ZnO) have been prepared by the reactive-environment, hollow cathode sputtering method.@footnote 1@ The use of Nb and W as effective dopants is reported for the first time. Metallic targets were used exclusively, and the dopant concentration was easily controlled using a second sputtering power supply. As a result of the cathode and gas flow geometry, the sputtering is conducted in metal mode, and the target and doping materials are free from oxidation during the deposition process. Film resistivities achieved with the various dopants will be reported. For In@sub 2@O@sub 3@:Mo, a resistivity of 1.6x 10@super -4@ @ohm@-cm and a mobility of 80 cm@super 2@/Vs were achieved for Mo concentrations in the range 0.5-5.0% as measured by ICP. XPS analysis indicates Mo with a +6 valence state. The dependences of film resistivity on substrate temperature during preparation and film temperature during measurement will be presented and discussed. Different dominant scattering mechanisms can be seen in different films. Reasonably transparent films of CuAlO@sub 2@ will be reported. And remarkably, semi-transparent films of InN having sheet resistances of 12 @ohm@/square have also been prepared. A scaled-up linear cathode 50 cm in length is under construction, and we expect to report results for ZnO:B deposited using this source. @FootnoteText@ @footnote 1@A. E. Delahoy, S. Y. Guo, C. Paduraru, and A. Belkind, J. Vac. Sci. Technol. A 22 Jul/Aug 2004.

4:00pm **TF-ThA7 High Efficiency CIGS Thin Film Solar Cells***, **K. Ramanathan**,* National Center for Photovoltaics **INVITED**

This paper will present the current staus of solar cells fabricated from CuInGaSe@2@(CIGS) polycrystalline thin films. CIGS thin film solar cells are considered as an excellent option for power generation at low cost. The technology has matured to the point of commercial production. We will highlight the special properties of CIGS materials and the 3-stage growth process developed at NREL. We have achieved a world-record solar cell efficiency of 19.3% at NREL. As the device efficiencies have increased and the confidence in the repeatability has grown, more attention is given to basic science of junction formation, surface properties of absorber films, and electronic properties of interfaces. We shall review our work in this area and also our collaborations with our industrial partners.

4:40pm **TF-ThA9 High Stability a-Si:H Films Deposited using Cluster-Suppressed Triode Plasma CVD***, **K. Koga**, N. Kaguchi, M. Shiratani, Y. Watanabe,* Kyushu University, Japan

Reduction of a total volume of amorphous silicon particles below 10 nm in size (clusters) incorporated into a-Si:H films is the key to suppression of light-induced degradation of the films, since the films containing the less volume of clusters show the higher stability.@footnote 1@ In order to realize such reduction, we have deduced a sticking probability s of clusters to a stainless steel mesh from an experiment for which gas containing clusters has been passed through a series of eight meshes. Most clusters are trapped with the first two meshes, indicating s~1. Based on the result, we have employed a cluster-suppressed plasma CVD reactor@footnote 2@ together with a triode discharge for which clusters are trapped with a mesh placed at 18 mm above a substrate. The light-induced degradation of the film qualities has been evaluated using a n@super +@Si/a-Si:H(1µm thick)/Ni Schottky solar cell. The initial and stabilized fill factor FF of the Schottky cell is 0.60 and 0.56, respectively. The degradation ratio of 6.7% is significantly low compared to the ratio of 17% for device quality films deposited using a conventional diode discharge. The stabilized FF= 0.56 surpasses the initial FF= 0.53 for the diode discharge. We will also present experimental results obtained using an "improved version" of the cluster-suppressed triode plasma CVD reactor. @FootnoteText@ @footnote 1@K. Koga, N. Kaguchi, M. Shiratani and Y. Watanabe, J. Vac. Sci. Technol. A 22, (2004) to be published.@footnote 2@M. Shiratani, K. Koga, M. Kai, and Y. Watanabe, Thin Solid Films 427, 1(2003).

Technology for Sustainability
Room 303D - Session TS-ThA

Fuel Cells for Clean Power, Hydrogen Storage

Moderator: R.L. Bersin, Emergent Technologies Corporation

2:00pm **TS-ThA1 Fuel Cells for Clean and Efficient Power Generation***, **S.C. Singhal**,* Pacific Northwest National Laboratory **INVITED**

Fuel cells provide a low- or no-pollution technology to electrochemically generate electricity at very high efficiencies using a variety of fuels. Use of hydrogen produced from renewable sources as fuel or direct use of biomass-derived fuels in fuel cells for transportation and power generation can contribute significantly to a truly sustainable global economy. In addition, fuel cell-based technologies that include carbon dioxide capture and sequestration are being developed to produce electricity with zero greenhouse gas emissions even with the use of hydrocarbon fuels. Several types of fuel cells have been under development in the last three decades for clean and efficient power generation; most prominent among these are the proton exchange membrane (PEM) and the solid oxide (SOFC) fuel cells. This presentation reviews the materials and performance of these two types of fuel cells and discusses the differences between them, particularly with respect to the fuel requirements. Status of these two types of fuel cells and key challenges associated with materials and electrochemistry are discussed, and directions for future research and development are presented.

2:40pm **TS-ThA3 Hydrogen Storage-A Critical Challenge to the Hydrogen Economy**, ***R.H. Jones,*** Pacific Northwest National Laboratory **INVITED**

Vehicle range on a single tank of hydrogen is critical for the economic viability of hydrogen fueled vehicles. A range of 500 kilometers is projected for economic viability and this requires the storage of 4 kg of H@sub2@. Compressed H2 tanks with a capacity of about 2 kg of H@sub2@ stored at 350 bar of pressure have been certified while tanks with higher capacity stored at 700 bar are being developed. Liquidified H2 tanks can store more H@sub2@ in a vehicle than compressed H@sub2@ but liquifying H@sub2@ requires considerable energy and boil-off of the liquid H@sub2@ is a concern, especially in enclosed spaces. Storage of H@sub2@ in bulk hydrides or on the surface of carbon or boron nitride nanotubes are attractive because of the low pressures involved. Recent studies have shown that NaAlH@sub4@ can be reversibly charged and discharged with H2 100's of times but the capacity of this hydride material is only about 1/2 of that needed. Storage of H2 on the surfaces of carbon nanotubes has shown great promise but verification of the storage capacities has not occurred. However, carbon nanotubes have the potential to store about 80% of the desired quantity of H@sub2@ so it remains a viable storage material. Generation of H@sub2@ by chemical reaction of a hydride such as LiH with water to produce H@sub2@ is also attractive because of the significant amounts of H@sub2@ that can be generated by this process. The key issues for this process of generating H@sub2@ is the need to reprocess the reaction products and the cost associated with transportation and reprocessing this product. There are several options for storing hydrogen on-board a vehicle but as summarized above considerable development work is needed before the hydrogen economy can be realized. Critical materials issues associated with H@sub2@ storage will be presented.

Friday Morning, November 19, 2004

Applied Surface Science
Room 210A - Session AS-FrM

FIB and Novel Ion Analysis Methods

Moderator: F.A. Stevie, North Carolina State University

8:20am **AS-FrM1 Elemental and Surface Analysis Via Focused Ion Beam Induced X-Rays***, **L.A. Giannuzzi**,* FEI Company

Characteristic X-ray emission result from ion/solid interactions, and is the basis for the well known analysis technique referred to as particle induced X-ray emission (PIXE). Characteristic X-rays may be emitted by either bombardment by MeV protons or heavy ions of a few keV. The advantage to heavy ions is that the X-ray yield is confined to a narrow region near the surface. Since the stopping power for < 30 keV Ga+ ions may be orders of magnitude greater than the stopping power for < 30 keV electrons, the acquisition of characteristic X-rays from regions containing both excellent spatial resolution and excellent depth resolution using a focused ion beam (FIB) instrument rather than a scanning electron microscope (SEM) as the primary source are feasible. An additional advantage of heavy ion induced X-ray emission over electron induced X-ray emission is that the Bremsstrahlung is orders of magnitude lower. Thus, ion induced X-ray spectra provides for superior peak to noise ratios, and therefore, offers the possibility for trace element sensitivity compared to electron induced X-ray emission via e.g., X-ray energy dispersive spectrometry (XEDS). In addition, the near surface ion/solid interactions also allow for the possibility of surface analysis via FIB induced X-ray analysis (FIBIX). An added advantage of the FIBIX technique is its sensitivity to soft X-rays, and therefore, light elemental analysis.

8:40am **AS-FrM2 FIB for Materials Characterization, Device Creation and Sample Preparation***, **R.J. Young**,* FEI Company **INVITED**

Focused ion beam (FIB) systems and DualBeam (combined FIB-SEM) systems have become key tools in the high-resolution characterization of materials, most notably in the semiconductor and data-storage industries, but also extending to many other disciplines where localized sample preparation and analysis is required. Site-specific cross-sections and transmission electron microscope (TEM) samples through disparate materials can be prepared using FIB milling. On a DualBeam the SEM can be used to directly monitor the sample preparation, allowing the section to be precisely positioned relative to a sub-surface feature that is exposed during the sample preparation. In addition, high-resolution, high contrast STEM (scanning transmission electron microscopy) imaging is possible with the electron beam, enabling more problems to be solved in the DualBeam without resorting to the TEM. Ion beam and electron beam induced gas chemistry is also possible, enabling the localized deposition of conductors and insulators, and the selective etching of materials. These capabilities are used in characterization applications for surface protection and delineation of cross-section faces, and also allow integrated circuits to be rewired to debug or prototype the device. Similarly, micro- and nano-scale devices can also be created or modified by the FIB/DualBeam, enabling rapid investigations into novel structures that would be impractical to create by other methods.

9:20am **AS-FrM4 High Spatial Resolution XPS Analysis of Focused Ion Beam Irradiated Specimens***, J.L. Fenton, **K.M. Archuleta**, J.E. Fulghum,* The University of New Mexico*; D.P. Adams, M.J. Vasile,* Sandia National Laboratories

Focused ion beams (FIB) are utilized in applications ranging from the preparation of samples for SEM and TEM analysis to machining of micro-tools. Despite their widespread use, there have been few detailed studies identifying how ion bombardment affects the chemistry of the near-surface region. The goal of this project is to assess the impact of Ga+ resulting from FIB preparation. High energy (30 keV) focused ion beam sputtering was first used to mill >100 µm wide features in Si, C and GaAs substrates. Both quantitative, high spatial resolution imaging and spectra-from-images methods were then used to characterize surface chemical distributions. The Ga distribution on the surface was determined in each case, and the impact of implanted gallium on surface oxidation was evaluated. The change in surface stoichiometry with ion dose (from approximately 10@super 15@ - 10@super 18@ ions/cm2) is also discussed. Atomic force microscopy and TEM have been used to investigate the evolution of morphology with ion dose so to aid the interpretation of XPS data.

10:20am **AS-FrM7 Examining the Impacts of Ion Sputtering on Nanoparticles and Nanoporous Materials***, **A.S. Lea**, M.H. Engelhard, D.J. Gaspar, J.R. Williams, D.R. Baer,* Pacific Northwest National Laboratory

Nanostructured materials of various types and forms are increasingly subject to every type of chemical and physical analysis possible. During the course of studies on several different types of nanostructured materials, we have observed evidence that the extent of damage and material removal rates due to ion sputtering may be significantly different than for continuous films or bulk forms of similar materials. To confirm such effects, we need to know many details about size, size distribution, density, and shape that are not always readily obtained. This presentation will review our efforts to quantify the sputter and damage rates for some nanomaterial systems, including iron oxide nanoparticles and porous silica films. We are working to expand our range of information in more details for these materials and to different types of nano-sized objects. Material removal rates are monitored by XPS and AES and material structure information, including material amounts, is also measured by a variety of methods including TEM, XRD and Nuclear Reaction Analysis.

10:40am **AS-FrM8 Determination of Optimum Depth-Resolution Conditions for Time-Of-Flight Medium Energy Backscattering***, **R.D. Geil**, B.R. Rogers, Z. Song,* Vanderbilt University

Measurements of depth resolution in time-of-flight medium energy backscattering analysis have been made in ErAs and ScAs single crystal films on GaAs (100) as a function of depth, beam energy, and analysis angle using He@super +@ as the analysis ion. Film thicknesses ranged from about 5 Å to 50 Å. Experiments were performed with beam energies ranging from 100 keV to 270 keV with the targets oriented at angles ranging from 5° to 55°. Multiple scattering and straggling effects limited depth resolution at analysis angles near 55° while the resolution of the spectrometer was the limiting factor for angles near normal to the beam. Estimates of depth resolution were made from theoretical calculations and were shown to be in good agreement with experimental values when the analysis angles were small. The departure of theoretical values from experimental measurements can be attributed to multiple scattering events and surface roughness.

11:00am **AS-FrM9 Quantitative Profiling of Thin Films by Means of Elastic Recoil Detection Analysis (ERDA) with High Energetic Heavy Ions***, **W. Bohne**, J. Röhrich, E. Strub,* Hahn Meitner Institut Berlin GmbH, Germany **INVITED**

Heavy-Ion ERDA (Elastic Recoil Detection Analysis) can be used to characterize thin solid layers. The concentrations of chemical elements can be determined as well as the layers' thickness and depth profiles. For the measurement, the sample is irradiated with a heavy ion beam. Atoms of the sample are recoiled and detected with an energy and mass dispersive spectrometer. Since the ERDA principle is based on the classical Rutherford scattering theory, the expected yields for the given conditions can be calculated exactly. Therefore, ERDA is a standard-free method. Absolute concentrations can be determined for all detected chemical elements simultaneously, including hydrogen, with almost the same sensitivity. With the time-of-flight ERDA setup at the Hahn-Meitner-Institut (HMI), there are measured almost 500 samples per year. As a standard projectile beam gold ions with an energy of 350 MeV are used. Typical requests are determination of the stoichiometry, in-depth element distributions, concentration of impurities, and the validation or calibration of data from other analytical methods. Typical artifacts or systematic uncertainties of these methods can be ruled out by comparison with the ERDA data. There will be presented a selection of current ERDA measurements mainly concerning the characterization of materials for thin film photovoltaic devices developed at the HMI. Also a comparison with other analytical methods will be shown. The pros and cons of ERDA measurements will be dicussed.

Biomaterial Interfaces
Room 210D - Session BI+MN-FrM

Bio-MEMS and Microfluidics

Moderator: J.J. Hickman, Clemson University

10:00am **BI+MN-FrM6 Creating Protein and Vesicle Arrays Using Designated Surface Chemistry in Combination with a Novel Microfluidic Pattering Device***, B. Niederberger, M. Dusseiller, D. Falconnet, B. Städler, G.L. Zhen, F. Rossetti,* ***J. Vörös***, ETH Zurich, Switzerland

Protein microarrays play a key-role in drug discovery, drug development and diagnostics by providing a highly sensitive, parallel analysis of the proteome of complex samples. The methods (e.g. spotting) that are currently available for the creation of DNA microarrays can not be directly used for proteins because they are subject to the loss of function upon contact with an ambient environment. In this work, we present a novel way to create arrays of different proteins or vesicles using a microfluidic device. The concept relies on a designated surface chemistry, which allows activation for subsequent binding events, in combination with crossing microfluidic channels for the local functionalization by separated laminar streams. Besides its simplicity and cost efficiency, this concept has the major advantage that it keeps the proteins in a hydrated environment throughout the experiment. The working principle of this arrayer is to activate spots by an activation stream and to do subsequent functionalization by reagent streams flowing perpendicular to the first stream. The surface pattern was provided by a MAPL-chip (Molecular Assembly Patterning by Lift-off) which consists of well defined areas (i.e. spots) of biotin or NTA functionalized PLL-g-PEG surrounded by a resistant surface of unfunctionalized PLL-g-PEG. The PDMS flow cell was fabricated by soft lithography and sealed to the sample surface by pressure. The position and the width of the streams containing the analytes could be adjusted using different flow rates in the microchannels. Fluorescent microscopy was used to monitor in situ the creation of a microarray consisting of alternating spots of streptavidin labeled with two different fluorophores. The concept was further extended to create heterogeneous arrays of his-tagged proteins and vesicles. This novel technique enables the creation of protein (including membrane-protein) microarrays in normal research labs in a simple and cost efficient way.

10:20am **BI+MN-FrM7 Polymeric Materials for DNA Sensing and Integration into Microfluidic Channels***,* ***R.A. Zangmeister****, M.J. Tarlov,* National Institute of Standards and Technology

Advances in microchip technology coupled with innovative bioassays are advancing the field of biosensing in microfluidics. We have previously reported a method for immobilizing single-stranded DNA (ss-DNA) probe molecules in polyacrylamide hydrogels within plastic microfluidic channels, creating a sensing matrix for target oligos. Spatially defined plugs are formed by photopolymerization of a solution containing 19:1 polyacrylamide/bisacrylamide and ss-DNA modified at the 5' end with an acrylic acid group. Low concentrations of ss-DNA targets can be electrophoresed into the hydrogels where complementary strands are captured by hybridization and are detected. We are interested in identifying and characterizing other polymeric materials that can be used as DNA sensing matrices for use in microchannel devices. Our goal is to identify polymeric materials that can be patterned within a microchannel, either by photochemical or electrochemical means, and that possess surface chemical groups that can be used to chemically graft probe oligos, or potentially other biological probe molecules, onto the surface. One such candidate that we are currently investigating is poly(3-aminophenol). Our strategy is to pattern a poly(3-aminophenol) thin film, modify it with probe oligos, and demonstrate a hybridization based DNA assay on that surface for use in a microfluidic format. We are able to selectively deposit poly(3-aminophenol) thin films onto gold electrodes under potential control. Surface pendant amine groups, as evidenced in infrared studies, allow for linkage of probe oligos to the polymer surface. Polymer deposition conditions, characterization, modification with probe oligos, and success of target hybridization detection will be discussed.

10:40am **BI+MN-FrM8 Cell Biology On a Chip: Elastomeric Microfluidic Platforms for Cell Culture Applications***,* ***A. Folch****,* University of Washington **INVITED**

The ability to culture cells in vitro has revolutionized hypothesis testing in basic cell and molecular biology research and has become a standard methodology in drug screening and toxicology assays. However, the traditional cell culture methodology - consisting essentially of the immersion of a large population of cells in a homogeneous fluid medium - has become increasingly limiting, both from a fundamental point of view (cells in vivo are surrounded by complex spatiotemporal microenvironments) and from a practical perspective (scaling up the number of fluid handling steps and cell manipulations for high-throughput studies in vitro is prohibitively expensive). The recent advances by our laboratory to address both limitations will be presented, including a microfluidic long-term cell culture platform that features cellular micropatterns and focal delivery of soluble factors to single cells. We are also developing elastomeric sensors and actuators for single-cell probing and manipulation by inexperienced users. These inexpensive technologies allow us to test novel hypotheses concerning neuromuscular development, chemotaxis, and neuronal axon guidance.

11:20am **BI+MN-FrM10 Ultrasensitive MALDI MS Analysis of Peptides Separated in an RF Plasma Polymer Modified Microfluidic Device***,* ***G.R. Kinsel****, X. Li,* University of Texas at Arlington

Rapid, information rich analysis of complex biological samples, such as the proteome of a given cellular system, represents a significant challenge for modern bioanalytical devices. A prototype open-channel microfluidic device under development in laboratory integrates an array of technologies available and/or developed in our laboratory to achieve efficient separation and ultrasensitive detection the components of peptide/protein mixtures. Specifically, separation of peptide mixtures is achieved through electroosmotic flow of the sample through 100 micron open-channels imprinted into a PMMA wafer. Modulation of the separation characteristics is achieved by either using the channels as formed or following coating of the channels by pulsed RF plasma polymerization of thin films having various chemical properties. Changes in peptide retention characteristics have been observed to correlate with changes in the column coating chemistry. Separation of simple mixtures can be achieved in minutes using this device. Following separation of the peptides, MALDI mass spectra of the isolated compounds is achieved by rastering the desorption / ionization laser down the open channel. This approach clearly allows the unambiguous assignment of the peptide molecular weight. In addition, because of the confinement of the sample to extremely small volumes, and the consequent high surface concentrations, extremely low limits of detection have been obtained for the separated peptides e.g. an LOD of 1.6 attomole of the peptide casomorphin has been observed. The coupling of this microfluidic device with MALDI mass spectrometry clearly holds enormous promise for substantially lowering the limits of detection and the requisite analysis time, while providing maximum information content for components in complex peptide / protein mixtures.

11:40am **BI+MN-FrM11 Measurement and Analysis of Changes in EOF with Protein Adsorption using the Dynamic Current Monitoring Method.***,* ***K. Lenghaus****,* Clemson University*; M.J. Tarlov, L. Locascio,* NIST*; J. Jenkins, S. Sundaram, S. Krishnamoorthy,* CFD Research Corporation*; J.J. Hickman,* Clemson University

The high surface to area ratio of MEMS devices places certain constraints upon their operation. One of these is that conventional, pressure driven flow is a relatively inefficient means of moving liquids through microfluidic channels, owing to the large backpressure encountered. The parabolic flow profile of pressure driven flow can also be undesirable in certain applications, especially in regards to sample separation and delivering analytes to detectors. Electro-osmotic flow (EOF), providing that conditions are conducive to its operation, can thus be a preferable option, since it doesnâ?Tt have the same problems with high backpressures, and its top hat flow profile, as shown by capillary electrophoresis, is well suited to separations and analysis. However EOF is sensitive to the type and density of electrical charges at the wall, and the adsorption of molecules or biomolecular species can substantially alter the EOF characteristics of the system. Using the dynamic current monitoring method, the change in EOF with protein exposure was tracked on the timescale of minutes, and the effect of changing the driving voltage, buffer composition, capillary surface and other parameters was obtained. Building on our previous protein adsorption work, we show that under some circumstances changes in EOF with exposure to different proteins can be extremely rapid. Whether or not desorption and recovery of the original EOF characteristics occurs depends on the specific protein/surface combination, as does the final EOF reached. The rates of adsorption and desorption were also determined using finite element analysis methods, compared with those obtained under pressure driven flow conditions, and a hypothesis of the method of interaction has been postulated.

Biomaterial Interfaces
Room 210D - Session BI-FrM
"Active" - Dynamic Biointerfaces

Moderator: S. Zauscher, Duke University

8:20am **BI-FrM1 The Effect of Cell Detachment Method on the Identity and Quantity of Residual ECM Proteins Retained at Surfaces***, **H.E. Canavan**, X. Cheng, B.D. Ratner, D.G. Castner,* University of Washington

Treatment of tissue culture polystyrene (TCPS) with poly(n-isopropylacrylamide) (pNIPAM) has been developed as a technique for the harvest of intact cell monolayers. Although low-temperature liftoff from pNIPAM is known to be less damaging to cells than traditional cell removal methods, little is known about the effects these techniques have on the underlying Extracellular Matrix (ECM). Recently, we demonstrated that although immunoassay of ECM components show that low-temperature liftoff removes the majority of the ECM concurrently with the cells, XPS and SIMS results reveal that some protein does remain at the pNIPAM surface. In this work, we further examine the effect that low-temperature liftoff from pNIPAM and traditional cell removal methods have on the ECM. Using XPS, we compare the relative amount of ECM remaining at culture surfaces after cell removal by the different methods. Using SIMS, MALDI, and immunostaining, we identify the individual proteins left behind. Finally, LDH assay is used to ascertain the viability of the residual ECM left behind by each cell removal method. We find that in addition to its dramatic effects on cell viability and morphology, trypsin removes much of the underlying ECM and often adsorbs to the surface itself, drastically reducing the adhesion of new cells. Although mechanical dissociation of the cell layer is less damaging to the underlying ECM, harvest via this method results in incomplete cell layers with partially damaged appearance. Of these techniques, only low-temperature liftoff from the pNIPAM surface harvests a complete cell monolayer while leaving behind ECM proteins capable of promoting new cell adhesion.

8:40am **BI-FrM2 Thermally Responsive Surfaces Formed by Plasma Polymerisation of N-Isopropyl Acrylamide***, **N.A. Bullett**,* University of Sheffield, UK, United Kingdom*; R.A. Talib, S.L. McArthur, R.D. Short, A.G. Shard,* University of Sheffield, UK

Temperature responsive surface coatings show great potential for a number of novel applications, such as 'smart' cell culture substrates for the control of cell attachment and detachment. Surface grafted N-isopropyl acrylamide (NIPAAm) has been shown to be suitable for this purpose, and the possibility of producing these coatings by deposition from plasma has been recently demonstrated by Pan et al.@footnote 1@ We find that, although it is possible to produce surfaces that demonstrate a temperature-dependent transition (as determined by contact angle goniometry and ellipsometry), there is a significant risk of delamination or solubilisation of the plasma polymers when they are in contact with water. In this work we demonstrate the importance of substrate temperature and discharge power on the properties of plasma polymerized NIPAAm. X-ray photoelectron spectroscopy (XPS) analyses were used to examine the composition of the deposited films, demonstrating that the high power deposits contain less characteristic functional groups (notably amides), indicating greater fragmentation of the monomer, and a high degree of cross-linking, whilst the low power deposit closely resembles conventionally polymerised NIPAAm. However, the very low power plasma polymers were shown, by XPS analysis and ellipsometry, to be unstable to rinsing with distilled water. The effect of substrate temperature during deposition was also investigated. It was found that higher substrate temperatures produced a more stable film at lower plasma powers. Useful films are therefore only produced within a narrow parameter space. The effect of using pulsed discharges and co-monomers was also investigated. We demonstrate that these plasma polymers can be patterned and used for cellular co-culture. @FootnoteText@ @footnote 1@ Pan YV, Wesley RA, Luginbuhl R, Denton DD, Ratner BD; Biomacromolecules 2001, 2, 32-36.

9:00am **BI-FrM3 Using Enzymes to Switch Surface Properties***, **R.V. Ulijn**,* University of Manchester, UK, United Kingdom*; M.R. Alexander, F.J.M. Rutten,* University of Nottingham, UK*; J.E. Gough, F. Carabine, J.L. Rutherford,* University of Manchester, UK

We study synthetic surfaces that change their properties upon biochemical stimuli (i.e. an enzymatic reactions). Surfaces that can be tuned (switched) to either bind or resist (biological) molecules or cells are desirable for a number of applications in the biomedical sciences. Enzymes are ideal tools for such surface engineering because they are highly selective and truly compatible with biology. We demonstrated that a peptide-hydrolyzing enzyme (chymotrypsin) could be employed to significantly alter the wettability of modified glass surfaces by hydrolysis of surface bound di-peptides. Here, we describe the use of XPS and ToF-SIMS analysis to characterise the changes in surface chemistry achieved using this approach. The methodology was applied in switching the attachment of cells to surfaces. A number of surfaces have been identified that are â?~stickyâ?T (promoting cell adhesion) or â?~non-stickyâ?T to certain cells. By using our biochemically responsive surfaces we demonstrate for the first time the possibility of switching between these two surface properties and therefore to switch cell adhesion in real time.

9:20am **BI-FrM4 Conformational Mechanics of Surface Grafted Stimulus-Responsive Polypeptides***, **A. Valiaev**, D.W. Lim, N. Abu-Lail, A. Chilkoti, S. Zauscher,* Duke University

Stimulus-responsive macromolecules have attracted significant research interest due to their potential applications in drug delivery, molecular motors, and nanoscale actuation devices. ELPs are stimuli-responsive biomacromolecules that undergo an inverse phase transition triggered by changes in solvent temperature, pH, or ionic strength. Associated with this transition is a significant conformational collapse and change in surface energy. To date, most research on ELPs has focused on the investigation of bulk properties and their aggregation behavior in solution. Our research is the first, we believe, to provide detailed insight into the mechanisms of elasticity and conformational mechanics of ELPs immobilized as ensembles on surfaces and on the single molecule level. First we performed single-molecule force spectroscopic experiments on elastin-like polypeptides (ELPs) that shed light on their time-dependent structural changes, physico-chemical and mechanical properties. We also present results obtained with a quartz crystal microbalance (QCM), cantilever deflection measurements, and adhesion force spectroscopy on surface immobilized ELP ensembles. QCM enabled us to study the effective mass change and the change in the mechanical dissipation behavior when ELPs collapse and swell as waters of hydrophobic hydration are released or consumed by the surface grafted protein. Experiments with micro-cantilevers decorated on one side with covalently grafted ELPs showed that a phase transition induces a considerable surface stress, leading to significant cantilever bending. Our approach promises to yield simple and sensitive bioanalytical devices, because cantilever bending can be easily measured. Lastly, adhesion force spectroscopy enabled us to quantify surface energetic changes associated with the phase transition behavior of surface grafted ELP ensembles.

9:40am **BI-FrM5 pH Induced Conformational Behaviour of Polyelectrolytes in Bulk Solution and Grafted to Surfaces: Neutron Reflectometry and Fluorescence Studies***, **M. Geoghegan**,* Univ. of Sheffield, UK, United Kingdom*; L. Ruiz-Perez, A.J. Parnell, J.R. Howse, A.J. Pryke, C.J. Crook, P. Topham, S.J. Martin, A.J. Ryan, R.A.L. Jones,* Univ. of Sheffield, UK*; A. Menelle,* Lab. Lön Brillouin, France*; J.R.P. Webster,* Rutherford Appleton Lab, UK*; I. Soutar, L. Swanson,* Univ. of Sheffield, UK

We present neutron reflectometry results on (deuterated) water-swollen poly[diethylamino)ethyl methacrylate] (PDEAMA, a polybase) and polymethacrylic acid (PMAA) brushes grafted from silicon substrates using atom transfer radical polymerisation. The PDEAMA data are presently the more comprehensive and reveal that the expanded brush (low pH) is some 6 to 10 times thicker than the collapsed brush at high pH. Brush data will be compared with bulk solution data of the collapse transition of PMAA in water measured by a variety of fluorescence techniques: steady state energy transfer, lifetime, and time-resolved fluorescence anisotropy measurements, which enable a correlation of this single polymer in solution collapse transition with the confinement-influenced transition which occurs when the polymers are tethered to a surface.

Magnetic Interfaces and Nanostructures
Room 304A - Session MI-FrM
Advanced Magnetic Data Storage and Thin Film Processing

Moderator: E. Dobisz, Hitachi

8:20am **MI-FrM1 Magnetic Tunnel Junctions for Magnetoresistive Random Access Memory***, **J.M. Slaughter**, J. Åkerman, B. Butcher, R.W. Dave, M. DeHerrera, M. Durlam, B.N. Engel, G. Grynkewich, J. Janesky, J. Martin, S.V. Pietambaram, N.D. Rizzo, K. Smith, J.J. Sun, S. Tehrani,* Freescale Semiconductor **INVITED**

Magnetoresistive random access memory (MRAM) employs a magnetoresistive device integrated with standard silicon-based microelectronics, resulting in a combination of qualities not found in other memory technologies. For example, MRAM is non-volatile, has unlimited read and write endurance, and has demonstrated high-speed read and write operations. Fundamentals of MRAM based on Magnetic Tunnel Junction (MTJ) devices, and recent technology developments in the areas of magnetic materials and magnetic device design is reviewed. The properties of our unique toggle-switching MRAM bit, as well as specific magnetic and electrical properties required for that bit will is discussed and compared to the conventional switching approach. The new bit cell uses a balanced synthetic-antiferromagnetic free layer and a phased write pulse sequence to provide robust switching performance with immunity from half-select disturbs. The use of this bit cell in a 4Mb MRAM circuit also is described.

9:00am **MI-FrM3 Processing Challenges in the Magnetic Recording Industry***, **J.A. Katine,*** Hitachi Global Storage Technologies **INVITED**

Following the introduction of the giant magnetoresistive sensor in 1997, the areal density of magnetic storage doubled annually for five years. This doubling meant that the critical dimension of the smallest features on the thin film recording head, the sensor trackwidth and the writer poletip width, decreased by 30 percent per year. Recently, though, there has been a dramatic slowdown in rate of increase for areal recording density, in large part due to the processing challenges associated with scaling the critical features to sub-100 nm dimensions. This talk will present an overview of the processing of magnetic recording heads, emphasizing the key challenges facing the industry. These include lithographic tooling options for printing critical dimensions that will soon be smaller than the smallest features used in IC processing. Of particular interest to the industry is the feasibility of using direct write electron beam lithography for the production of recording heads. Another obstacle to overcome will be developing etching techniques for magnetic materials that do not produce unacceptable damage at the edges of the devices. Advances are also required in developing the thin insulating gap materials with thermal and electrical properties suitable for ultrahigh areal density recording. In addition to processing challenges in the recording head, to reach areal densities approaching 1 Terabit per square inch, it is likely that the magnetic media itself will require lithographic patterning. I will outline the formidable challenges involved in producing economically viable patterned media.

10:00am **MI-FrM6 Reversal Mechanism of Patterned Co/Pd Multilayer Islands***, G. Hu, T. Thomson,* Hitachi Global Storage Technologies*; C.T. Rettner,* IBM Almaden Research Center*; **B.D. Terris,*** Hitachi Global Storage Technologies

Arrays of patterned Co/Pd magnetic islands with perpendicular anisotropy and sizes ranging from 30nm to 5 microns have been fabricated and characterized. Applying a field along the easy axis results in individual magnetic islands switching as a single unit, as observed by the magnetic optic Kerr effect and magnetic force microscope (MFM) measurements. The angle dependence of switching closely resembles the behavior predicted by the Stoner-Wohlfarth model with a minimum in island coercivity at 45 degrees. These results are expected for small islands which may reverse by rotation, but are surprising for the larger islands. The nominally identical continuous film exhibits a completely different behavior, where the film coercivity increases with the angle (t) between the applied field and film normal as 1/cos(t), as predicted for domain wall motion controlled reversal. These data leads to a model whereby the reversal of the larger islands is controlled by a nucleation event, followed by a rapid wall motion. The observed switching field of the island is the switching field of the small nucleation site, which reverses coherently. To test this model, we artificially introduce nucleation sites into the islands by applying an in-plane field. This results in a domain wall motion controlled angle dependent behavior in all islands capable of supporting a multi-domain ground state (size ranging from 200nm to 5 microns). The reversal behavior of the larger islands therefore depends on the initial state of the islands. In an island with no nucleation sites the reversal is governed by rotation, whereas in the same island into which nucleation sites have been pre-created, the reversal is governed by wall motion.

10:20am **MI-FrM7 Hierarchical Self-Assembly as a Route to Future Magnetic Data Storage***, **S.B. Darling,*** Argonne National Laboratory*; D. Sundrani, S.J. Sibener,* The University of Chicago

A novel hybrid top-down/bottom-up approach is used to hierarchically organize magnetic nanoparticles on the nanoscale. Lithographically prepared substrate channels direct the self-assembly of a high-aspect ratio diblock copolymer template resulting in nearly defect-free alignment over arbitrarily long distances.@footnote 1@,@footnote 2@ Selective wetting of the channel sidewalls by one block initiates the organization and is followed by coarsening until the entire channel volume contains aligned domains. Overfilling the channels further extends the alignment, originally nucleated on the sidewalls, both above and beyond the confined space. This approach may be useful for globally aligning domains across an entire surface with the top interface being nearly flat despite the corrugated substrate underneath. The oriented structures are surprisingly defect-tolerant, accommodating roughly 10% variations in channel width without introducing disclination or dislocation defects. The laterally alternating nanoscale structure of the diblock film is then used to template the adsorption of FePt nanoparticles. Attractive interaction of the nanocrystal capping molecules with one of the polymer blocks leads to nearly 100% selective adsorption. Hybrid hierarchical approaches such as this are promising candidates for high density storage media. @FootnoteText@ @footnote 1@ D. Sundrani, S.B. Darling, S.J. Sibener, Nano Letters, 4 (2004) 273-276.@footnote 2@ D. Sundrani, S.B. Darling, S.J. Sibener, Langmuir, In Press.

10:40am **MI-FrM8 Enhanced Magnetic Moment in Iron Nitride Thin Films***, **R.A. Lukaszew,*** University of Toledo, US*; D. Pearson, Z. Zhang,* University of Toledo

In magnetism, maximum interest is focused on iron and iron-based alloys because these materials are of greatest practical use. Iron-based alloys are most susceptible to modification by nitrogen, which can turn them from weak to strong ferromagnets. Nitrogen enters 3d metals as an interstitial provoking a dilation of the lattice. The Fe-N system exhibits several phases of technological importance including several Fe-N intestitial compounds with nitrogen ordering. The ordered iron nitrides are metastable compounds which can persist at moderate temperature because of kinetic constraints. In particular, the magnetic properties of the @alpha@"-Fe@sub 16@N@sub 2@ phase have been of interest for both scientists and technologists since it was first discovered to exhibit magnetization as great as 2.4 T, significantly higher than that of @alpha@-Fe. An important issue is the role of nitrogen in enhancing the iron magnetic moment. Current theories explain the enhanced magnetic moment in terms of a reduced moment on the iron sites that are the nearest-neighbours of nitrogen, and an enhanced moment on the more distant sites due to hybridisation of the 3d states of the iron that is a nearest neighbour and charge transfer from the more distant iron @footnote 1@. No polarization of the N atoms is assumed. In order to evaluate the potential of these materials for magnetic recording head as well as to understand the origin of the observed enhanced magnetic moment more detailed research is required. We will present our studies on epitaxial FeN films grown using reactive magnetron sputtering. We will show magnetic characterization of the films, performed using SQUID, MOKE and XMCD. In particular XMCD data indicates that in addition to Fe, N is also polarized in these films. Thus we believe that N polarization may be the primary reason for enhanced magnetic moment in these materials. @FootnoteText@ @footnote 1@. J.M. D. Coey and P. A. I. Smith, J. Mag. Mag. Mat. 200, 405-424 (1999).

11:00am **MI-FrM9 Direct Observation of Nano-Oxide Formation in Spin Valve Multilayers***, **A.T. McCallum,*** NIST, U.S.*; S.E. Russek,* NIST

The addition of thin oxide layers, that specularity reflect electrons, to spin valve trilayers has been shown to increase the giant magnetoresistance of these structures. Usually the specularity of an oxide is deduced by comparing the resistance and magnetoresistance of samples with and without nano-oxide layers. These comparisons are clouded by sample to sample variations and the fact that adding an oxide changes the growth mode of material deposited on top of the oxide. In-situ conductance measurements allow direct observation of the specularity increase as the oxide forms. One key advantage of this measurement is that on one sample the effects of a range of oxygen exposures are measured. The Co free layer of bottom pinned spin valves was oxidized and the conductance and magnetoconductance were measured. These measurements show that the CoO@sub x@ layers become specular within ~5 monolayers of oxygen exposure. Conductance measurements during the oxidation of relatively thick layers of Co show a specularity increase of at least 0.10. Subsequent oxidation does not change the specularity of the nano-oxide. RHEED patterns taken during the oxidation show the appearance of a new face centered cubic, fcc, 111 lattice with a lattice constant consistent with CoO. The region between these two lattices is probably the region that determines the amount of specularity at that interface with the nano-oxide. A second set of bottom pinned spin valves were made with a 1 nm thick Co@sub 1-x@Fe@sub x@ cap on the free layer. This material was then exposed to oxygen. One nm should be about the amount of metal oxidized. The more Fe that was included in the free layer cap the less the specularity increased with oxygen exposure. The sample with a Co cap had a increase in the magnetoconductance of 0.00020 @ohm@@super -1@ during oxidation. The sample with a pure Fe cap had a decrease in magnetoconductance of 0.00005 @ohm@@super -1@ with oxidation.

11:20am **MI-FrM10 Novel Green Plasma Etch Chemistries for Magnetic Metals.**, ***A.S. Orland***, *A.A. Dyachenko, R. Blumenthal,* Auburn University

Chlorine, an enviromental menace, is traditionally used to etch magnetic metals in manufacturing of semiconductor devices. In this work, the etching of magnetic metals with hydrogen plasmas containing environmentally friendly gases such as carbon monoxide, carbon dioxide and cyclopentadiene (Cp) is investigated by means of supersonic pulse, plasma sampling mass spectrometry. Previous results, in our group,@super 1@ have indicated that the etch rates of nickel are significantly enhanced in CO/H@sub 2@ plasmas and CO@sub 2@/H@sub 2@ plasmas at the same time that formate and oxalate signals appear in the mass spectrum. It is further assumed that these species serve as new primary etchants resulting in the formation of volatile metal formates and oxalates. The etch rates and chemical mechanisms responsible for the etching in CO/H@sub 2@, CO@sub 2@/H@sub 2@ and Cp/H@sub 2@ plasmas will be presented. @FootnoteText@ @footnote 1@ A.Orland, Ph.D. thesis, Auburn University, 2003.

11:40am **MI-FrM11 Characterization of FePt-based Magnetic Nanocomposite Thin Films Prepared by Pulsed Filtered Vacuum Arc Deposition**, ***Y.W. Lai***, *M.F. Chiah, N. Ke, Q. Li, W.Y. Cheung,* Chinese University of Hong Kong; *S.P. Wong,* Chinese University of Hong Kong, Hong Kong

We have prepared FePt-X (X = C, Cu or Ag) nanocomposite thin films of various compositions consisting of FePt grains embedding in carbon, copper or silver matrices using a pulsed filtered vacuum arc deposition technique. In addition to usual co-deposition processes, another process was adopted where multilayers of the three elemental components with an appropriate design of thickness and sequence were first deposited followed by a rapid thermal annealing (RTA) in an argon atmosphere. Characterization of these films was performed using Rutherford backscattering spectrometry, x-ray diffraction, transmission electron microscopy, and vibrating sample magnetometry. The dependence of the structure and magnetic properties, such as the phase and size of the magnetic grains and the coercivity of these films, on the deposition parameters, annealing conditions and the matrix materials were studied in details. Both x-ray diffraction and transmission electron microscopy analyses confirmed the formation of L1@sub 0@ phase FePt nano-grains after appropriate annealing. For example, for the film with a particular composition of Fe@sub 43@Pt@sub 45@Cu@sub 12@, the L1@sub 0@ phase formation was observed after the RTA process at 400@super o@C, and the film exhibited a coercivity of 6.5 kOe. Compared to films prepared by usual co-deposition process, those films prepared using the multilayer deposition approach see a significant lowering in the ordering temperature at which the L1@sub 0@ phase started to form. The degree of lowering in the ordering temperature was seen to depend on the species of the matrix material. It is believed that different mechanisms are responsible for such ordering temperature lowering in films of different matrices. This work is supported in part by the Research Grants Council of Hong Kong SAR (Ref. Number: CUHK4216/00E).

Nanometer-scale Science and Technology
Room 213D - Session NS-FrM

Nanometer-scale Structures

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

8:20am **NS-FrM1 Peter Mark Memorial Award Presentation: Nanometer-Scale Fabrication Techniques for Building Semiconductor Devices**, ***K. Guarini***[1], IBM T. J. Watson Research Center **INVITED**

Integrated circuit performance improvements have been achieved largely by aggressive shrinking of the silicon transistor and metal interconnect dimensions. Future technology generations will require even greater innovation to continue the performance trend. New materials, device structures, and integration schemes will all play roles in advancing CMOS technology. Novel nanometer-scale patterning techniques will be critical to this success. This talk will give an overview of nanometer-scale patterning needs of the semiconductor industry and highlight several novel solutions. Direct write scanning probe lithography (SPL) is a high-resolution patterning technique that uses a sharp tip in close proximity to a sample to pattern nanometer-scale features. Low energy electrons field emitted from a probe tip can be used to expose polymer resists with sub-30-nm resolution and nanometer-scale alignment registration. In comparison to electron beam lithography, SPL has wider exposure latitude, improved linearity, and reduced proximity effects. Material self assembly provides an alternative means for pattern formation at the nanometer-scale. With feature sizes defined by fundamental molecular properties, self assembly can access dimensions and densities beyond the capabilities of conventional patterning techniques. Our work has focused on identifying and demonstrating key applications of self assembly. In one example, we enhanced the capacity of thin film metal-oxide-semiconductor devices using nanostructured electrodes patterned by self assembly. We have also demonstrated the use of material self assembly in facilitating continued scaling of non-volatile FLASH memories. These high resolution patterning processes offer innovative solutions to existing challenges in microelectronics and are well suited to enabling enhanced device performance and functionality by augmenting the available tool kit for manufacturing.

9:00am **NS-FrM3 Self-assembled Multilayers Creating Tailored Resists for Nanostructure Fabrication**, ***M.E. Anderson***, *E.M. Carter, A.R. Kurland, C. Srinivasan, M.W. Horn, P.S. Weiss,* The Pennsylvania State University

Designing and patterning complex hierarchical assemblies by exploiting methods of directed self-assembly in combination with a variety of lithographic techniques has been an active area of research for patterning in the sub-100 nm regime. We have used self-assembled multilayers to create molecular ruler resists to define nanostructures with precise spacing and edge resolution reaching the nanometer-scale.@footnote 1-3@ A molecular ruler resist of self-assembled multilayers, composed of alternating layers of @alpha@,@omega@-mercaptoalkanoic acids and coordinated metal ions, is selectively deposited on initial lithographically defined gold structures. This resist can be tuned based on the number of layers deposited to a desired thickness (routinely between 10-100 nm). Then, metal is deposited on the sample and the resist is removed, yielding spacings between metal structures dependent on the dimensions of the tailored resist. Work is underway to build molecular ruler resists independently either by capping selected regions of growth or by orthogonal growth of two different multilayer systems. A scheme in development is electroless metal deposition of the secondary metal, where the ruler resist both defines the structure spacing and inhibits deposition for selective metal placement. Molecular ruler resists can withstand the rigors of lithographic processing and are being developed to advance this method toward device fabrication. @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).

9:20am **NS-FrM4 Studies of Self-Assembling Bilayers for Layered Nanofabrication (LNF)**, ***T.-Y. Shih***, *A.A.G. Requicha, M.E. Thompson, B.E. Koel,* 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 we have called layered nanofabrication (LNF). We report on the embedding of gold nanoparticles in several layers of octadecyltrichlorosilane (OTS) deposited on a SiO@sub2@ surface. Atomic force microscopy (AFM) was used in ex-situ studies of the formation of self-replicating bilayers with hydrophobic-hydrophilic properties and hydrogen bonding as triggered by treatments using acetone. Analysis of the Au nanoparticles after several bilayer-by-bilayer growth cycles showed that they decreased in apparent height and roughness according to the number of deposited layers. Ellipsometry was used to monitor the OTS film thickness and characterize the film growth mode. We were able to achieve a controllable, stepwise linear growth of a flat, multilayer film that eventually produced a high-quality, planarized nanoparticle-containing surface.

9:40am **NS-FrM5 Cross-sectional Ballistic Electron Emission Microscopy Studies of Molecular Beam Epitaxy Grown Quantum Wells**, ***C. Tivarus***, *J.P. Pelz, M.K. Hudait, S.A. Ringel,* The Ohio State University

Schottky diodes formed on GaAs quantum wells grown by Molecular Beam Epitaxy are studied using Cross-sectional Ballistic Electron Emission Microscopy (XBEEM), in order to determine the influence of quantum confinement and pinning effects on Schottky barrier (SB) formation. The

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

diodes were formed by both in-situ and ex-situ gold deposition on cleaved sides of heterostructures composed of a sequence of GaAs quantum wells (QW) separated by AlGaAs barrier layers. Using this technique, we were able to determine the local SB height for each QW. We found that the SB height increases with decreasing the QW thickness d@sub QW@ , varying from ~0.91 eV for d@sub QW@ @>=@ 9 nm to ~1.04eV for d@sub QW@=1 nm. This dependence will be discussed in terms of the QW confinement energy as well as reduced pinning effects at the QW/metal interface. We will also compare XBEEM samples made by in-situ vs. ex-situ metal deposition to clarify the role of chemical treatment and of an interfacial oxide layer on the SB formation. Additionally, the cross sectional configuration offered a direct measure of electron beam spreading due to scattering inside the metal film, as a function of film thickness. This spreading was surprisingly large, with full width at half maximum spreading of ~16 nm (~23 nm) for a 4 nm (7nm) thick Au film. The measurements will be compared with model simulations to quantify inelastic and elastic hot-electron scattering processes in the bulk and at the interfaces of the metal film, and to gain insight into the controversial issue of whether lateral momentum is conserved during hot electron transport over a metal/semiconductor interface. Work was supported by NSF and Office of Naval Research.

10:00am **NS-FrM6 Defect Mediated Transport in Nanostructures by Scanning Impedance Spectroscopy***, **R. Shao**, M.P. Nikiforov, J. Vavro, D.A. Bonnell,* The University of Pennsylvania

Defects and interfaces can dictate the transport properties of macroscopic structures and completely dominate the behavior of nanostructures. We have shown that Scanning Impedance Microscopy (SIM) can be used to determine local electronic structures of scattering centers in nanotubes/wires and the perturbing effect of atomic interfaces on local continuum properties. This talk will combine SIM and low temperature transport measurements to quantify the effect of defects on transport in individual nanofibers and at atomically abrupt oxide interfaces in SrTiO@sub 3@ bicrystals. In the latter case we have found a defect induced phase transition at low temperature.

10:20am **NS-FrM7 Supramolecular [60]Fullerene/Porphyrin Assemblies on Metals***, **H. Spillmann**,* University of Basel, Switzerland*; D. Bonifazi,* ETH Zürich, Switzerland*; A. Kiebele, H.-J. Güntherodt,* University of Basel, Switzerland*; T.A. Jung,* Paul Scherrer Institute, Switzerland*; F. Diederich,* ETH Zürich, Switzerland

The unique electrochemical and photophysical properties of porphyrin and [60]fullerene compounds makes them promising candidates for the construction of two- and three-dimensional organic-based materials. An important question is how pristine C60 and self-assembled monolayer of porphyrin arrays will organize on surfaces. Self-assembly of electron-rich flat aromatic molecules such as porphyrins shall enable the selective formation of electron donating monolayer, which can be covered by pristine C60. The chromophore interaction between the electron donor (porphyrin) and acceptor (C60) should enhance a supramolecular multilayer structure. Herein, we report first Scanning-Tunneling-Microscopy investigations of the behaviour of several porphyrin derivatives on metal surfaces wherein single porphyrin molecules are forcefully arranged in self-assembled monolayer. The specific properties of the single porphyrin derivatives make such molecularly modified surfaces suitable candidates for patterned surfaces to allocate fullerenes. Consequently, first nanostructures based on the interaction of the fabricated porphyrin-based assemblies with fullerene molecules will be presented.

10:40am **NS-FrM8 Synthesis and Optical Characterization of Gold Nanoplates***, C.S. Ah, **W.S. Yun**, D.H. Ha, K.J. Kim,* Korea Research Institute of Standards and Science, Korea

We report on a high-yield synthesis and optical characterization of gold nanoplates. The nanoplates were prepared by controlled reduction of hydrogen tetrachloroaurate with reduced amount of sodium citrate in the presence of poly(vinyl pyrrolidone). The plates have a shape of either triangle or truncated-triangle of around 10@super 4@ - 10@super 5@ nm@super 2@ in area with a thickness of about 20 - 30 nm. High-resolution TEM analysis reveals that the individual plate is a single crystal with well-developed flat {111} facets. Optical spectra of the nanoplates show distinctive plasmon absorption bands which can be attributed to their highly-anisotropic shape. The optical characteristics are strongly dependent upon the size of the gold nanoplates. In particular, the absorption band in NIR region, which is believed to originate from the longitudinal dipole plasmon resonance, dramatically shifts to red when the planar size of the plate increases. We hope that this gold nanoplate should serve as an excellent platform for molecular self-assembly and as a useful building-block in developing new-materials and devices.

11:00am **NS-FrM9 Non-Spherical Metal Nanoparticles: Tuning Optical Properties by Controlling Structure***, **J.S. Shumaker-Parry**, H. Rochholz, F. Stefani, W. Knoll, M. Kreiter,* Max Planck Institute for Polymer Research, Germany

Gold colloids have been studied extensively due to the dependence of their optical properties on colloid size, interparticle spacing, and local dielectric environment. Recently there have been efforts to prepare non-spherical nanoparticles because of their unique electronic, optical and other physical properties. We have fabricated novel non-spherical metal nanoparticles by combining colloidal lithography, metal film evaporation and ion beam milling. This process produces a large number of metallic nanoparticles on a surface with uniform size and identical orientation in parallel, a major advantage compared to electron beam lithography methods. Gold and silver quartermoon and c-shaped nanoparticles have been fabricated. A finite element method was applied to classical electrodynamics for two-dimensional models of these nanoparticles in order to understand the optical characteristics. These calculations predict large electromagnetic field enhancements that are localized or uniformly distributed, depending on the nanoparticle structure. We have characterized the optical properties of the nanoparticles using extinction scattering cross section spectroscopy and single-particle light scattering spectroscopy. We show that the optical properties of the nanoparticles can be tuned by changing the size of the colloid mask and by controlling the opening of the c-structure.

11:20am **NS-FrM10 Elucidation of the Electronic Properties of Immobilized Alkanethiolate-Stabilized Gold Clusters and Nanoparticles Using Scanning Tunneling Microscopy***, P.S. Weiss, **R.K. Smith**, S.U. Nanayakkara, B.A. Mantooth, G. Woehrle,* The Pennsylvania State University*; J.E. Hutchinson,* University of Oregon

The single electron transport properties of metal nanoparticles have led to great interest in their potential integration into nanoscale electronics. Here, we discuss and compare the electronic characteristics of isolated, solution-derived, and ligand-stabilized gold clusters (Au@sub 11@L@sub 10@) and nanoparticles (Au@sub 101@L@sub 43@), taken in both cryogenic (4 K, UHV) and ambient conditions using scanning tunneling microscopy and spectroscopy. The clusters and particles (d@sub CORE@ = 0.8 nm and 1.5 Â± 0.5 nm, respectively) are immobilized on alkanethiolate self-assembled monolayers with inserted dithiol molecules. We thoroughly characterize the self-assembled monolayer surface to which the nanostructures are attached with both local probes and ensemble measurements. At low temperature, the Au@sub 11@ clusters demonstrate Coulomb blockade behavior, with zero-conductance gaps resulting from quantum size effects.

11:40am **NS-FrM11 Optical Properties of Ordered Arrays of Vanadium Dioxide Nanoparticles***, **R. Lopez**, J.Y. Suh, R.F. Haglund Jr., L.C. Feldman,* Vanderbilt University

Arrays of vanadium oxide nanoparticles with long-range order have been fabricated by pulsed laser deposition in an arbitrary pattern defined by focused ion-beam lithography. Interaction of light with the nanoparticles is controlled by the geometrical arrangement as well as by the differing optical properties displayed by the metallic and semiconducting phases of VO@sub 2@. The particle arrays present a previously unknown scattering resonance in the blue region of the spectrum. The scattering is pronounced in the semiconductor phase, but is less intense and slightly blue-shifted in metallic state. This phenomenon is intrinsically interesting, since previous studies of VO@sub 2@ switching have been confined to the IR region, whereas this configuration produces the relevant optical effects of the transition in the visible spectrum. In addition, the transition to the metallic state does not exhibit the usual step function at the critical temperature. Instead, the scattered light begins to increase in intensity at 68°C, the temperature of the bulk phase transition, and reaches a maximum before falling to a lower value in the metallic state resulting in a anomalous double loop hysteresis. This transient scattering enhancement results from the order-disorder transition that occurs as the nanoparticles are transformed by random fluctuations. The disorder or inhomogeneity present during this process enhances the scattering by coherent contributions of length scales longer than the array lattice constant, the necessary additional Fourier components to describe a disordered system. Arrays such as this open up new opportunities to study surface plasmon interactions for nanoparticles in close proximity, with the added advantage that the interaction can be switched on by the thermally driven metal-semiconductor phase transition in VO@sub 2@.

Plasma Science and Technology
Room 213C - Session PS+BI-FrM

Plasmas in Bioscience

Moderator: K. Seaward, Agilent

8:20am **PS+BI-FrM1 X-Ray and Neutron Reflectivity Studies of Plasma Polymer Coatings***, S.K. Øiseth,* Unaffiliated*; P.G. Hartley, **K.M. McLean**,* CSIRO Molecular Science, Australia*; A Nelson, M James,* Bragg Institute, Australia

Plasma polymer coatings adhere to and contour the surfaces of most organic and inorganic materials, and are attractive as surface chemical modification systems, since they offer both robustness and inherent surface chemical functionality for further surface chemical derivatisation. A variety of different techniques have been used to characterise the physico-chemical properties of surfaces of plasma polymer films. In many cases, however, it is also desirable to probe the internal structure of both modified and unmodified plasma polymer coatings in order to optimise their properties for a given application.. Reflectometry techniques are now becoming increasingly important in the characterization of nano-scale structured interfaces. X-ray reflectivity in particular is ideally suited to the study of the internal properties of layered film structures on surfaces, yielding data concerning sub surface structure and material properties. Neutron reflectivity meanwhile offers the ability to characterise surface layers in aqueous environments. In this study heptylamine and allylamine plasma polymer coatings were prepared on silicon wafers, and analysed using X-ray reflectometry before and after further surface modification procedures (e.g. adsorption of protein species from solution). Surface chemistry of the coatings was characterised using X-ray photoelectron spectroscopy (XPS). Atomic force microscopy (AFM) was also used to characterise both roughness and local film thickness at step-edges on the films. The excellent reflectivity data obtained demonstrate the suitability of plasma polymers for reflectivity studies (primarily due to their low surface roughness). Preliminary experiments on plasma polymer layers using neutron reflectivity are also described, which highlight the effect of surface hydration on layer properties.

8:40am **PS+BI-FrM2 Angle Resolved XPS Characterisation of Plasma Polymerised Chemical Gradients***, K.L. Parry,* Plasso Technology Ltd.*; A.G. Shard,* University of Sheffield, United Kingdom, UK*; R.G. White,* Thermo Electron Corporation, UK*; J.D. Whittle,* Plasso Technology Ltd.*; **A. Wright**,* Thermo Electron Corporation, United Kingdom, UK

Well-defined chemical gradients are potentially important materials in a wide range of research activities. The surfaces of such materials can be derivatised with differing functional groups to provide spatially resolved surface chemical properties. Such surfaces can, for example, be used to immobilise biomolecules, which may become a route to producing novel biosensors. This study is concerned with chemical gradients within thin layers of plasma co-polymers deposited onto glass substrates. Continuous gradients of chemistry (hydrocarbon to either acid or amine) are produced by carefully programming the composition of the plasma monomer mixture while varying the area of the substrate exposed to the plasma. It will be shown that spatially resolved XPS is an ideal tool to determine the composition of the near surface region as a function of distance along the chemical gradient. Parallel angle resolved XPS provides additional information about the uniformity of the layer with depth. Such measurements can show, for example, surface enrichment of one of the functional groups in the co-polymer layer or variations in thickness along the chemical gradient. It is therefore possible to construct chemical state and thickness line scans or maps from the same ARXPS data set. Such data provide valuable information regarding the plasma co-polymer deposition process.

9:00am **PS+BI-FrM3 Surface Characterization of Plasma Processed Bio-Functional Micro-Patterned Polymeric Surfaces***, **A. Valsesia**, M. Manso, M. Kormunda, P. Colpo, D. Gilliland, G. Ceccone, F. Rossi,* EU-JRC-IHCP, Italy

The functionalization of the material surfaces is one of the major requirements for the control of the biological response and for the improvement of the biocompatibility. Among the functionalization techniques, PE-CVD is of high importance since the control of the film properties is achieved by an accurate modulation of the plasma processing parameters. PE-CVD allows the synthesis of a wide spectrum of bio-functional polymers: acid/base fouling surfaces (PAA, PAL) and super-hydrophilic anti-fouling surfaces (PEG, PEG-like coatings). Moreover the combination of plasma deposition and plasma etching techniques allows the formation of micro and nano-patterned surfaces with contrasted functionalities. In this work we have studied the plasma deposition of PAA (COOH functional), PAL (NH2 functional) and PEG-like (anti-fouling) layers. The chemical surface characterization of the films has been performed by XPS and TOF-SIMS and the surface free energies components have been calculated by Contact Angle in static and dynamic mode. QCM provided the evaluation of the mechanical stability of the samples in buffer solutions as well as the calculation of the bio-activity of the surfaces in proteins absorption experiments. The surface topography of the samples has been investigated by AFM. The micro-patterned surfaces have been characterized by TOF-SIMS and XPS in imaging mode, revealing the capability of the plasma processing techniques to produce chemically contrasted micrometric motives. The bio-response (protein absorption and cell adhesion) of the micro-patterned samples is under study.

9:20am **PS+BI-FrM4 Plasma Sterilisation and De-pyrogenation of Surfaces: Review and Analysis of Mechanisms***, F. Rossi, R. De Mitri, M. Hasiwa,* European Commission Joint Research Centre, Italy*; S. Bobin, R. Eloy,* Biomatech, France*; T. Hartung,* European Commission Joint Research Centre, Italy*; **P. Colpo**,* EU-JRC-IHCP, Italy

Mechanisms of plasma sterilisation are reviewed and analysed in terms of radiation induced desorption, UV radiation effects and etching. Different plasma discharges are analysed with Optical Emission Spectroscopy in order to find optimum conditions of UV emission and radicals production. Those effects are compared and related to effective sterilisation and depyrogenation rates obtained from the literature and experimentally on Bacillus subtilis and LPS. It is shown that UV emission is the major contribution for sterilisation and chemical etching for depyrogenation. SEM analysis of spores at different times of treatment show the degradation of the outer shell, as well as size and coverage reduction as the treatment duration increases. Effects of plasma on pyrogen is illustrated by AFM and ToF SIMS. A strategy for optimised sterilisation and depyrogenation treatment is proposed.

9:40am **PS+BI-FrM5 Plasma Processes for Micro- and Nano-Patterning Biomedical Polymers***, **P. Favia**,* University of Bari, Italy **INVITED**

Low pressure plasma processes can tune chemical composition, surface energy and topography of most substrates of biomedical interest in a well controlled way. Among the wide range of plasma-modification procedures, micro- and nano-patterning plasma-deposition processes of thin coatings are among the most interesting and novel technologies aimed to drive the behaviour of cells on surfaces. Two kind of plasma procedures will be described in this contribution, and some interesting in vitro tests will be discussed. The first one consists in the deposition of "cell-repulsive" coatings through physical masks to produce patterned surfaces; here "cell-adhesive" domains are alternated to non-adhesive ones. The second process involves the deposition of teflon-like coatings of CF@sub x@ chemical composition, including randomly distributed surface features with nanometric dimensions, which are peculiar of certain deposition conditions in modulated regime. Acknowledgments This research has been developed in the framework of the MIUR-FIRB RBNE01458S_006, COFIN '99 "Biomaterials with micro- and nano- structured surfaces" and 'NANOMED' QLKE-CT-2000 projects, whose financial contribution is gratefully acknowledged.

10:20am **PS+BI-FrM7 Novel Plasma Modification of Microfluidic Devices for Control of Electroosmotic Flow***, **E.R. Fisher**, C.S. Henry, M.A. Boggs, I.T. Martin, Y. Liu, C.D. Garcia,* Colorado State University

Microchip capillary electrophoresis (CE) is a widely used separation technique that combines the efficiency of CE with the portability of a microchip. Poly(dimethylsiloxane), PDMS, is often used to fabricate these microfluidic devices because it is inexpensive, has good optical properties, and the fabrication of complicated channel geometries is straightforward. Separations that occur in PDMS are based on the electroosmotic flow (EOF) within the channel. This, in turn, depends on the density of negatively charged groups on the PDMS surface, which is sensitive to both the pH of the solution and the sealing method (air plasma treatment, methanol). An additional issue is the hydrophobicity of the PDMS, which leads to the adsorption of hydrophobic analytes such as proteins during separations. The goal of this work is to treat PDMS with both non-depositing and depositing plasmas and fully characterize the altered surface chemistry, and its effects on EOF and separations. We have used depositing plasma systems to alter preassembled PDMS microchips, yielding novel surface chemistries. Plasma treated PDMS has been characterized using various surface analysis techniques, including contact angle measurements and XPS. XPS mapping shows that fluorocarbon (FC) plasma treatments permeate the channel via the reservoirs, not through the porous PDMS.

Consequently, the reservoirs and channel are selectively coated with a FC film, resulting in reduced EOF. Conversely, plasma deposition of a hydrophilic hydrocarbon film yielded an increase in EOF. Selected coatings are stable over multiple EOF measurements. Separations conducted with treated chips evaluate biomolecule fouling characteristics. This is the first report of the modification of these devices via depositing plasma systems; plasma treatment of PDMS microchips has essentially been limited to O@sub 2@ or air plasmas to oxidize or cure the PDMS, for the enhancement of adhesion of PDMS to PDMS/glass.

10:40am **PS+BI-FrM8 Thiol-Based Plasma Polymer Coatings as Platforms for Biosciences Applications***, **P.G. Hartley**, S.K. Øiseth, T.R. Gengenbach, G. Johnson, K.M. McLean,* CSIRO Molecular Science, Australia

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, for example, to enhance biocompatibility or to introduce defined chemical functionalities at interfaces for the subsequent coupling of bioactive molecules have seen their widespread application in the field of biomaterials research. We report on the development of sulphur containing plasma polymers using ethanethiol as the feed monomer. In order to ascertain the influence of deposition conditions on the properties of the films, a range of protocols were employed. The films were characterised by X-ray photoelectron spectroscopy (XPS); atomic force microscopy; streaming potential and contact angle measurements. Since XPS data are not sufficiently specific to distinguish between similar carbon-sulphur functional groups (e.g. thiol vs. sulphides), the nature and density of the surface functionalities were quantified by using a thiol specific maleimide containing probe. The stability of the films was tested by assessing coating thickness and chemistry before and after autoclaving. The effects of ageing in air, particularly with respect to the chemical structure were monitored over several months. The incorporation of sulphur functionalities provide reproducible supports for the subsequent grafting of proteins and for the adhesion of gold nanoparticles. The coatings were also shown to act as supporters of cell attachment and growth.

11:00am **PS+BI-FrM9 The Low Damage Surface Modification of the Self-assembled monolayer by the N@sub 2@ Neutral Beam Irradiation***, **Y. Ishikawa**,* Tohoku University, Japan*; T. Ishida,* National institute of Advanced Industrial Science and Technology, Japan*; S. Samukawa,* Tohoku University, Japan

For the realization of future organic molecular devices, controlling surface property of molecular film, such as the electric properties of organic molecule, is quite important. To improve surface property of molecular film, fine surface modification method is highly expected. Thus, we propose the method for controlling the surface properties of organic films by applying plasma process. For this purpose, we used our nearly developed the neutral beam system.@footnote 1@ The system could prevent the charged particles and ultraviolet photons, and only the neutral particles were irradiated to the substrates. In this study, we irradiated the N@sub 2@ neutral beam to the robust self-assembled monolayers (SAMs) made from terphenyls@footnote 2@ on the gold substrate as the first attempt for neutral beam system to the organic molecular thin films. Energy of the N@sub 2@ neutral beams are at the highest 10 eV. We compared the X-ray photoelectron spectra of terphenyl SAMs before and after the N@sub 2@ beam irradiation. Then the C-N bonds were generated by the beam irradiation with maintaining the surfer molecular structure. This result indicates that the surface of the terphenyl SAMs would be replaced from carbon or hydrogen to nitrogen, and we can expect that the electric properties of the organic materials would be drastically changed by this method. @FootnoteText@ @footnote 1@ S. Samukawa, K. Sakamoto, and K. Ichki: Jpn. J. Appl. Phys., Part 2 40, L779 (2001)@footnote 2@ T. Ishida, M. Sano, H. Fukushima, M. Ishida, and S. Sasaki: Langmuir, 18, 10496 (2002).

Plasma Science and Technology
Room 213A - Session PS1+DI-FrM

High K and Difficult Materials Etch

Moderator: A. Miller, LAM Research

8:20am **PS1+DI-FrM1 Inductively Coupled Plasma Etching of Poly-SiC in SF6 Chemistries***, **S.H. Kuah**, P.C. Wood,* SAMCO International Inc.

A study was made to find a low cost and robust etching solution for silicon carbide (SiC) using a commercially available inductively coupled plasma etching tool. Sulfur hexafluoride (SF6) was selected because of its high degree of F dissociation and non-hazardous nature. A parametric study of the etching characteristics of poly-SiC in inductively coupled plasma (ICP) SF6 chemistries was performed. Etch chemistry was found to greatly affect etch rate, selectivity, final surface cleanliness and smoothness. Etch rates as high as 5884 Å/min were achieved with high SiC/Cr selectivity (36) and clean, but relatively rough etched surfaces (134 Å RA) using a SF6/CF4/He gas mixture. It was found that He addition apparently increases the ionization of SF6 in the plasma and thus increases the SiC etch rate due to increases in the SF3+ and F radical concentrations@footnote 1,2@. The formation of pillar-like structures and side wall deposition was observed on the etched SiC surfaces under some conditions. These unwanted etch by-products exhibited a high concentration of Cr and Fluorine. However, an Ar plasma pre-clean of the the substrate, or high ICP and/or bias powers, and CF4 addition can reduce the pillars formation significantly. @FootnoteText@ @footnote 1@ J.D.Scofield, B.N.Ganguly, and P.Bletzinger, J.Vac.Sci.Technol. A 18, 2175 (2000).@footnote 2@ Z.A.Talib and M.Saporoschenko, Int. J. Mass Spectrom. Ion Processes 116, 1(1992).

8:40am **PS1+DI-FrM2 A Study of Inductively Coupled Plasma Etch of GaN/InGaN Based Light Emitting Diodes***, **H.D. Chiang**, K.C. Leou,* National Tsing Hua University, Taiwan, ROC*; C.H. Shen, S. Gwo,* National Tsing Hua University, Taiwan*; M.H. Wu,* Uni Light Technology Inc., Taiwan*; C.H. Tsai,* National Tsing Hua University, Taiwan

Group III-Nitride semiconductors are of considerable interest because of their potential for optoelectronic applications such as light-emitting diodes (LEDs) and laser diodes (LDs) in the visible light regions. The dry etching process is one of the critical steps in the fabrication of nitride-based LEDs. A study based on Taguchi experimental design was carried out to investigate the etch characteristics of GaN/InGaN quantum well light emitting diodes using a high density inductively coupled plasma of BCl@sub3@/Cl@sub2@-based chemistry. The process parameters studied include inductive power, bias power, BCl@sub3@/Cl@sub2@ gas ratio and chamber pressure. The etch characteristics measured were etch rate, surface roughness, side-wall angle and etch selectivity to SiO@sub2@ mask. It was found that the variations in the bias power had maximum effect on the etch rate whereas the pressure affected etch rate the least. Anisotropic profiles were generally achieved over a wide range of parameters with low substrate bias. Certain interesting phenomena such as grass and sidewall striations were observed. Nearly smooth etched surface were observed for most etch conditions. The etch mechanisms of different etch conditions on both GaN grown by MBE and MOCVD and the differences of surface roughness before and after etching will also be discussed.

9:00am **PS1+DI-FrM3 High-k Materials Etching***, **D. Wu**, B. Ji, S.A. Motika, E.J. Karwacki, M.J. Plishka,* Air Products and Chemicals, Inc.

As integrated circuit (IC) device geometry shrinks, high-k materials are needed to maintain adequate breakdown voltage. Due to their high chemical inertness and extremely low volatility, removal of the high-k materials has been technically challenging. In this paper, we will present an effective plasma etching process where a mixture of BCl3 and NF3 is identified as the reactive gas. Compared to pure BCl3, the etch rate for HfO2 was doubled after adding 25% NF3 to BCl3, and the etch rate for HfSixOy was also doubled after adding 15% NF3 to BCl3. Pure BCl3 did not etch ZrO2 at a condition of 0.55 W/cm2 power density and 500 mTorr chamber pressure. But an etch rate of 6 nm/min was achieved when using a mixture of 20% NF3 in BCl3. Detailed experimental setup and data analysis will be reviewed in this paper.

9:20am **PS1+DI-FrM4 Ion-Enhanced Plasma Etching of Metal Oxides in Chlorine Based Plasmas***, **D. Ramirez**, Y. Ta, 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-90nm 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@ 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, Hf@sub 1-x@Al@sub x@O@sub y@. The dominant etch products of Al and Hf metals in Cl@sub 2@ and BCl@sub 3@ plasmas were metal chlorides. However, the dominant etch products of Al@sub

2@O@sub 3@ and HfO@sub 2@ in Cl@sub 2@ and BCl@sub 3@ plasmas were metal chlorides and metal boron-oxy-chlorides, respectively. These results allowed us to assess 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. Enhanced surface chlorination of the metal oxide surfaces was observed with increasing ion energy, which demonstrates that the etching reaction is limited by the momentum transfer from the ions to the film surface. The etch rates of Al@sub 2@O@sub 3@ and HfO@sub 2@ and their selectivities to Si were found to increase in BCl@sub 3@ plasmas due to the increased oxygen removal rate. Etching of Hf@sub 1-x@Al@sub x@O@sub y@ will also be presented, with a focus on predicting its etch rate based on the etching of Al@sub 2@O@sub 3@ 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 Al@sub 2@O@sub 3@ and Hf@sub 1-x@Al@sub x@O@sub y@ in chlorine based plasmas will be discussed.

9:40am **PS1+DI-FrM5 Investigation of Etching Properties of HfSiO and HfSiON as Gate Dielectrics*, J.H. Chen,*** *W.S. Hwang,* National University of Singapore*; W.J. Yoo,* National University of Singapore, Singapore*; S.H.D. Chan,* National University of Singapore

Hf based high-K dielectrics have been studied as the alternative gate dielectric. For the high performance logic device application, HfSiON is receiving significant attention as the most promising dielectric material because of its good thermal stability, immunity to boron penetration and high carrier mobility in the channel under the gate. In advanced HfSiON films, N profile is optimized: the top HfSiON is highly nitrided to block boron penetration, but the bottom near Si substrate remains as HfSiO to maintain high carrier mobility in the channel. We investigated the etching properties of Hf@sub x@Si@sub 1-x@O@sub 2@ (x=0, 0.3, 0.5, 0.7 and 1) and their nitrided films in ICP of Cl@sub 2@/HBr/O@sub 2@. Results show that etch rates of HfSiO and HfSiON increase rapidly with increasing ion energy, ion density and ratio of Cl@sub 2@. Linear dependency of etch rates on the @sr@E@sub ion@, which obeys the universal energy dependency model of ion enhanced chemical etching yields, was observed with the etch threshold energies of 30-36 eV for HfSiO with different Si% in Cl@sub 2@/HBr. Etch rates of HfSiO and HfSiON are strongly dependent on the open area of the wafer because the oxygen released from these films can suppress the etching process. The addition of the small amount of O@sub 2@ to Cl@sub 2@/HBr plasma or increasing pressure can suppress the etching of HfSiO and HfSiON effectively. The 6nm thick HfSiO or HfSiON can be removed by a wet chemical of 1% HF (DHF) in 30s before anneal; after 700@super o@C anneal, etch rates drop slightly but the densified HfSiO interfacial layer (IL) of ~1nm cannot be removed in DHF. By incorporating N by the plasma nitridation, this IL can be removed by DHF in 10s, and very little Si substrate recess and clean surface can be achieved. This combined approach of the plasma etching and the wet removal proved that HfSiON can be integrated into advanced CMOS processes successfully.

10:00am **PS1+DI-FrM6 Etching of HfO@sub 2@ and HfSiO@sub x@ at Elevated Temperatures*, M. Hélot*,** CNRS, France*; G. Borvon, T. Chevolleau, L. Vallier, O. Joubert,* LTM-CNRS, France*; P. Mangiagalli, J. Jin, Y.D. Du, M. Shen,* Applied Materials

In CMOS technology, the traditional SiO@sub 2@ used as gate dielectric is being replaced by a material presenting a higher dielectric constant (so called high-K materials) for the 65 or more likely the 45 nm nodes. In the integration of such materials, the etch process is one of key issues since the volatility of etch by-products is low and the high-K/Si selectivity seems extremely difficult to achieve. This work is dedicated to the etching of HfO@sub 2@ and HfSiO@sub x@, two of the most promising candidates, using an industrial inductively coupled plasma source (ICP) with a hot cathode (the temperature range of the wafer can be adjusted from 200 to 350°C). Vertical high-K profile without footing or silicon recessing have been achieved. AFM measurements of silicon surface show an acceptable substrate roughness after etch. The etch process has to be adjusted with respect to the deposition technique (CVD vs. ALD) as well the thickness of the silicon oxide buffer layer between the silicon substrate and the high-K layer. XPS analyses reveal that the selectivity is obtained thanks to the formation of a thick C and Cl overlayer on SiO@sub 2@ and not on HfO@sub 2@. Even for these very thin layers, the endpoint techniques such as emission spectroscopy and spectroscopic ellipsometry have to used. Finally we found that the etch process (etch rate and uniformity) depends on the walls reactor seasoning.

10:20am **PS1+DI-FrM7 Ion-enhanced Etching of HfO@sub2@ with Cl@super+@, BCl@subx@@super+@(X = 1, 2) and SiCl @subx@@super+@(X = 1, 2,3) Ion*, K. Karahashi,*** MIRAI-ASET, JAPAN*; N. Mise,* MIRAI-ASET, Japan*; T. Horikawa,* MIRAI-ASRC/AIST, Japan*; A. Toriumi,* MIRAI-ASRC/AIST, Univ. of Tokyo, Japan

As advanced high-k gate dielectrics are being developed to replace SiO@sub2@ in the near future generation of microelectronics devices, understanding their plasma etch characteristics becomes vital for introducing new materials into the manufacturing process. We report on the interactions of HfO@sub2@ with ionic species contained in plasma etching environments. To clarify the ion induced reactions of Cl@super+@, BCl@subx@@super+@(X = 1, 2) and SiCl@subx@@super+@ (X = 1, 2,3), we employed the mass-analyzed ion beam apparatus that can irradiate a single ionic species to the sample surface under an ultra-high vacuum condition. Etching yield of SiCl@sub3@@super+@ ion is about 2 times larger than that of Cl@super+@ ion, and etching products are hafnium chlorides and oxygen atom. This result suggests that chlorine atoms play a key role in etching reaction, and that the chemical etching yield increases with increasing number of chlorine atoms contained in the incident ions. The kinetic energy of etching products, which were estimated by the time delay of etching products with respects to the incident ion pulses, was larger than 0.1 eV. Therefore, products are different from thermally desorbed molecules. This indicates that desorption is caused by the momentum transfer to hafnium chloride. This work was supported by NEDO.

10:40am **PS1+DI-FrM8 Evaluation of the Effectiveness of H@sub 2@ Plasmas in Removing Boron from Si After Etching of HfO@sub 2@ Films in BCl@sub 3@ Plasmas*, C. Wang*,** *V.M. Donnelly,* University of Houston

Etching of high dielectric constant ("high-K") materials in BCl@sub 3@-containing plasmas is challenging due in part to boron residue that deposits on the underlying Si or SiO@sub 2@ surface during the over-etching period. Boron is a p-type dopant and therefore it is best if it is removed prior to subsequent processing. We have investigated the effectiveness of H@sub 2@ plasmas in removing this boron-containing layer. Following etching of HfO@sub 2@ or Al@sub 2@O@sub 3@ thin films in a high-density BCl@sub 3@ plasma, including a 60s overetch period, samples were transferred under vacuum to a UHV chamber equipped with x-ray photoelectron spectroscopy (XPS). After observing B-coverages of ~1 x 10@super 15@ (equivalent of ~ 1 monolayer), the samples were transferred back to the plasma reactor for exposure to the H@sub 2@ cleaning plasma, and then re-examined by XPS. Optical emission spectroscopy was used to monitor B deposition on and removal from the plasma chamber walls. B deposition on the reactor walls during BCl@sub 3@ plasma exposure reached saturated coverage in ~2 min. Following this, the H@sub 2@ plasma removed half of this B layer in 90s, and 90 % in 320 s. B was rapidly removed (< 5s) from the BCl@sub 3@-over-etched Si surfaces provided that the walls were first cleaned in the H@sub 2@ plasma, with the Si sample held in the UHV chamber during the chamber cleaning process. Conversely, it took much longer (~170s) to remove all detectable B on the sample surface if the sample and the reactor chamber walls were cleaned in the H@sub 2@ plasma at the same time. Etching rates of SiO@sub 2@ and Si in the H@sub 2@ cleaning plasma will be reported. Mechanisms of B deposition on and removal from chamber walls and Si and SiO@sub 2@ surfaces will be discussed. A less effective sequential O@sub 2@/H@sub 2@ plasma cleaning process will also be presented. Supported by SRC and AMD Inc.

11:00am **PS1+DI-FrM9 Selective Etching of HfO@sub 2@ High-k Dielectric over Si in C@sub 4@F@sub 8@/Ar/H@sub 2@ Inductively Coupled Plasmas*, K. Takahashi*,** *K. Ono, Y. Setsuhara,* Kyoto University, Japan

As integrated circuit device dimensions continue to be scaled down, increasingly strict requirements are being imposed on plasma etching technology. Regarding gate dielectrics, the technological challenge continues for growing ultrathin SiO@sub 2@ films of high quality; however, the ultimate solution relies on high dielectric constant (k) materials. In integrating high-k materials into device fabrication, an understanding of the etching characteristics of the materials is required for their removal and for contact etching. This paper presents the etch rates and possible etch mechanisms for HfO@sub 2@ thin films on Si substrate in inductively coupled plasmas containing mixtures of CF@sub 4@/Ar/H@sub 2@ and C@sub 4@F@sub 8@/Ar/H@sub 2@, as a function of gas composition and rf bias power. In the experiments, the discharge was established at a gas pressure of 20 mTorr and an rf source power of 280 W. The gas flow rates of fluorocarbon and Ar were 2.5 and 247.5 sccm (the ratio of fluorocarbon to total was 1 %). The rate of H@sub 2@ was varied between 0 and 16 sccm. As the dc selfbias voltage was maintained at the constant value of -90 V, HfO@sub 2@ and Si were etched in the CF@sub 4@/Ar/H@sub 2@ plasma with no relation to H@sub 2@ flow rate. In the C@sub 4@F@sub 8@/Ar/H@sub 2@ plasma, however, the conditions could be found where HfO@sub 2@ was etched at the rate more than 10 nm/min, and the fluorocarbon polymer deposited on Si. In this regime, it can be possible to selectively etch HfO@sub 2@ over Si. The chemical composition of the polymer was carbon-rich, and the carbon content on HfO@sub 2@ was not so much as on the polymer. It can be said that carbonized products may correspond to etch products for HfO@sub 2@. @FootnoteText@ This work was supported by NEDO/MIRAI Project.

11:20am **PS1+DI-FrM10 Characterization of the Sputtering Process in an rf Plasma for the Patterning of Nonvolatile Materials***, **T.J. Kropewnicki**, A.M. Paterson, T. Panagopoulos, J.P. Holland,* Applied Materials, Inc.

With the integration of nonvolatile materials into microelectronic devices, such as NiFe in magnetic random access memory, perovskites in ferroelectric random access memory, and HfO@sub 2@ as a transistor gate dielectric, it has become necessary to develop methods of characterizing the patterning of these materials. Removal of these nonvolatile materials by sputtering with heavy ions is probably a key component of the etching mechanism. Sputtering of materials by ion bombardment has typically been characterized using high energy ion beam systems, leading to sputtering yield probabilities as a function of ion energy. Since typical commercial plasma etch reactors use rf power to energize the ion bombardment, the usefulness of these sputtering probabilities in understanding the reaction mechanism is limited by the much lower energy levels being produced by the rf sheath, and by the spread of ion bombardment energies typically produced by an rf plasma sheath. Ion energies less than 1000 eV are common in many plasma etch systems. To create a more realistic picture of the etching process, direct measurements of the actual rf waveforms occurring on the wafer are transformed using a simple plasma sheath model into ion energy distribution functions which are then used in combination with the reported sputtering yield data to predict more accurate sputter yields for these conditions. Langmuir probe measurements of ion fluxes are then used to determine the etch rates. Comparison of these predicted rates and actual measured rates will be presented as well as possible reasons for discrepancies between the two rates.

Surface Science
Room 210B - Session SS1-FrM
Hydrated Surface Phenomena

Moderator: E. Stuve, University of Washington

8:20am **SS1-FrM1 Wetting and Dissociation of Water on Cu(111) and Cu(110)***, **T. Schiros**, H. Öström, K. Andersson, O. Takahashi, L.G.M. Pettersson,* Stockholm University, Sweden*; A. Nilsson, H. Ogasawara,* Stanford Synchrotron Radiation Laboratory

A fundamental understanding of the factors that control the interaction of water metal surfaces is indispensable in predicting electrochemical interactions and pathways for dissociation. Here we address the adsorption of water on Cu(111) and Cu(110) using x-ray absorption and x-ray photoelectron spectroscopy experiments combined with density functional theory calculations. We have found that water adsorbs intact on both surfaces, and wets Cu(110) by forming a monolayer prior to ice formation. In contrast, water does not wet Cu(111), but rather forms three-dimensional ice-like clusters upon adsorption. Our calculations show a much weaker electrostatic interaction and a stronger Pauli repulsion with the oxygen lone pair on Cu(111) compared to Cu(110). We have also investigated how these factors affect the wetting capabilities of water on other metals. We discuss the influence of the d-band density of states with respect to the Fermi level.

8:40am **SS1-FrM2 Point Defects in a Partially Dissociated Wetting Layer: D@sub 2@O/Ru(0001)@footnote 1@***, **P.J. Feibelman**,* Sandia National Laboratories

Ab-initio total energies imply that about 43% of the D@sub 2@O molecules in a first layer on Ru(0001) optimally dissociate to adsorbed OD+D. This compares favorably to new x-ray photoemission measurements,@footnote 2@ which say that (3Â±0.25)/8 of them do. In the optimal wetting layer structure, atop sites on roughly 6% of the outer-layer Ru atoms are available as a natural pathway for D-adatom transport. They represent a surface analog of L-type, Bjerrum defects.@footnote 3@ An equal percentage of the wetting layer's H-bonds, disrupted by the presence of a second D atom, represent the corresponding D-type defects. @FootnoteText@ @footnote 1@ Supported by the USDOE, Office of Basic Energy Sciences, Division of Materials Sciences. Sandia is operated by the Lockheed-Martin Company under USDOE Contract No. DE-AC04-94AL85000.@footnote 2@ J. Weissenrieder, A. Mikkelsen, J.N. Andersen and P. J. Feibelman and G. Held (unpublished).@footnote 3@ N. Bjerrum, Kong. Dansk. Vid. Sels.Mat.-fys. Medd. 27, 1(1951).

9:00am **SS1-FrM3 Diffusion of He in Amorphous Solid Water: Observation of an Inverse H/d Lattice Isotope Effect***, **J.L. Daschbach**, G.K. Schenter,* Pacific Northwest National Laboratory*; P. Ayotte,* University of Sherbrooke, Canada*; R.S. Smith, B.D. Kay,* Pacific Northwest National Laboratory

The diffusion of He through amorphous solid water (ASW) has been measured in H@sub 2@O and D@sub 2@O between 50 K and 125 K. He is embedded in a thin layer of ASW grown on Pt(111) at 25 K by molecular beam techniques and subsequently capped with an ASW cap of precise thickness. Linear temperature programmed desorption of the embedded He diffusing through the ASW cap is measured by mass spectroscopy. We find that He diffuses more rapidly in D@sub 2@O than in H@sub 2@O ASW. To our knowledge, this is the first observation of a lattice isotope effect in diffusion. A microscopic kinetic model for He hopping between cage sites in the ASW, reflecting at the Pt(111) interface, and desorbing at the vacuum interface closely fits the data. The diffusion kinetic parameters are found to be D@sub 0@ = 1.3 ± 0.3 x 10@super -3@ cm@super 2@/s, E@sub a@ = 11.9 ± 0.17 kJ/mole and D@sub 0@ = 0.8 ± 0.2 x 10@super -3@ cm@super 2@/s, E@sub a@ = 11.2 ± 0.17 kJ/mole, for H@sub 2@O and D@sub 2@O respectively. The origin of this inverse isotope effect in the host lattice has been studied using transition state theory. These results indicate the inverse isotope effect arises predominantly from the frustrated rotations of the lattice water molecules.

9:20am **SS1-FrM4 H@sub 2@O/D@sub 2@O Dimer Formation on Pd (111) Studied by STM***, **E. Fomin**, M. Tatarkhanov,* University of California at Berkeley*; D.F. Ogletree, M. Salmeron,* Lawrence Berkeley National Laboratory

We have studied the adsorption and dynamics of H@sub 2@O and D@sub 2@O molecules and dimers on Pd(111) using variable low temperature (@>=@ 25 K) scanning tunneling microscopy (STM). At higher temperatures (>35K) dimers are formed by thermally activated diffusion. At lower temperatures dimer formation was induced by inelastic ecletron tunneling. We measured the hopping rate of single molecules and dimers and discovered that diffusion coefficients differ by 4 orders of magnitude. Recent theoretical analysis@footnote 1@, proposed to explain this effect implies isotopic change in a diffusion coefficient for D@sub 2@O dimers compared to H@sub 2@O ones. In our experiments we were unable to detect this difference. @FootnoteText@ @footnote 1@Ranea VA. Michaelides A. Ramirez R. de Andres PL. Verges JA. King DA. Water dimer diffusion on Pd{111} assisted by an H-bond donor-acceptor tunneling exchange - art. no. 136104. [Article] Physical Review Letters. 9213(13):6104, 2004 Apr 2.

9:40am **SS1-FrM5 Ultrafast Electron Solvation Dynamics and Structure of the Water/Metal Interface***, **M. Wolf**,* Free University Berlin, Germany **INVITED**

The dynamics of excess electrons in water is of fundamental importance for charge transfer and solvation processes in chemistry and biology. We have studied the ultrafast dynamics of photoinjected electrons into thin layers of amorphous ice grown on metal surfaces (Cu(111) and Ru(0001)) and probe the subsequent electron localization, solvation and transfer processes by femtosecond time- and angle-resolved photoemission spectroscopy.@footnote 1@ The solvation dynamics is observed directly through a transient increase of the electron binding energy, which occurs on a 100 fs to 1 ps time-scale and depends critically on the structure of the ice. On the other hand, exceptionally long-lived and highly localized electrons are formed in crystalline ice. As the structure of the solvent can be modified in a controlled way by the growth conditions and substrate our approach provides insights on the relation between structure and solvation dynamics in low dimensional systems. We have also used vibrational sum-frequency generation (SFG) spectroscopy, isotope scrambling experiments and work function measurements to investigate the structure of D@sub 2@O on Ru(0001).@footnote 2@ Our results suggest that the first bilayer consists of intact water molecules, while density functional theory predicts a half-dissociated structure as energetically most favourable state.@footnote 3@ Some explanations for these controversial findings will be discussed. @FootnoteText@ @footnote 1@C. Gahl et. al, Phys. Rev.

Lett. 89, 107402 (2002); U. Bovensiepen et al., J. Phys. Chem. B 107, 8706 (2003); Israel. J. Chem. (in press)@footnote 2@D.N. Denzler et al, Chem. Phys. Lett. 376, 618 (2003).@footnote 3@P.J. Feibelman, Science 295, 99 (2002).

10:20am **SS1-FrM7 Interfacial Segregation of Halogen Ions in Alkali Halide Solutions***, **S. Ghosal,*** University of California, Irvine*; B.S. Mun, D.F. Ogletree, M. Salmeron,* Lawrence Berkeley National Laboratory*; J.C. Hemminger,* University of California, Irvine

In recent years Molecular Dynamics (MD) Simulations@footnote 1, 2@ of alkali halide solutions have predicted the surface segregation of polarizable halogen ions. This is of particular interest since the composition of the liquid/vapor interface of salt solutions has implications for heterogeneous atmospheric chemistry involving sea salt aerosols@footnote 3@. We present here results from our studies of the surface composition of saturated salt solutions. Using a novel high pressure photoelectron spectroscopy (HPPES) system at beamline 9.3.2 of the ALS synchrotron radiation source, we have compared the surface composition of KBr and NaCl crystals cleaved in vacuum with the surface composition of the saturated solutions formed at the deliquescence point, in equilibrium with water vapor. Our results show that the anion/cation ratio in the saturated solution is significantly enhanced within one nanometer of the surface. This is consistent with the predictions of Jungwirth et al@footnote 1, 2@ regarding halogen surface segregation. @FootnoteText@ @footnote 1@ Jungwirth, P.; Tobias, D. J. J. Physical Chemistry 2002, 106(2), 379.@footnote 2@ Jungwirth, P.; Tobias, D. J. J. Phys. Chem. B 2002, 106, 6361.@footnote 3@ Finlayson-Pitts, B. J.; Hemminger, J. C. J. Phys. Chem. 2000, 104(49), 11463 .

10:40am **SS1-FrM8 Measurements of Interfacial Water Properties as a Function of Surface Functionalization Using the IFM***, **G.E. Thayer,*** Sandia National Laboratories, US*; A.K. Boal, B.I. Kim, J.E. Houston, B.C. Bunker,* Sandia National Laboratories

Water exhibits dramatically different structures and properties near interfaces, impacting a wide range of activities including the assembly and properties of nano- and bio-materials, microfluidic and sensor systems. In this work, we use the interfacial force microscope (IFM) to study forces generated by hydrophobic/hydrophilic surfaces in contact with water and the resulting properties of the near-surface water region. The IFM measures force-distance curves between a scanning probe tip and substrate surfaces, providing quantitative measurements of adhesion, long-range (electrical double layer) and short-range (Van der Waals and hydration) forces, and fluid properties such as viscosity. Measurements are performed at the water-solid interface as a function of surface and tip functionalization using self-assembled monolayers (SAMs), temperature, speed, and tip size. Our results indicate that in extreme cases a viscous water layer can form which extends greater than 5 nm from the surface is 6 orders of magnitude more viscous than bulk water. This remarkable effect is due to the interaction of surface hydration forces with the hydrogen-bonding network of water. Such forces are capable of controlling phenomena such as protein adsorption, for example we find forces generated by ordered interfacial water are large enough to resist adsorption of the motor protein kinesin.

11:00am **SS1-FrM9 Light-Induced Contact Angle Switching on Nanowire Surfaces***, **S.T. Picraux,** R. Rosario, T. Clement, J.L. Taraci, J.W. Dailey, D. Gust, A.A. Garcia, M. Hayes,* Arizona State University

We combine monolayer surface chemistry with silicon nanowire substrates to create a lotus leaf like surface, and for the first time demonstrate the amplification of light-induced water contact angle switching. Si nanowires are grown by the vapor-liquid-solid growth technique and the air oxidized surfaces are functionalized with tert-butyldiphenylchlorosilane and perfluorooctyltrichlorosilane, followed by 3-aminopropyldiethoxymethylsilane, to which a photochromic spiropyran molecule was attached. Measurements of the contact angle for water on both the smooth and nanowire surfaces allow direct estimation of the effects of surface morphology on hydrophobicity. Functionalized nanowire surfaces with contact angles above 90° on the smooth surface exhibit superhydrophobic behavior, whereas those with smooth surface angles below 90° exhibit superhydrophilic behavior. Spiropyran-functionalized surfaces show reversible photoswitching of the contact angles. When irradiated with UV light (366nm) the spiropyran is converted from a closed, nonpolar form to a highly polar open form. Visible light (450-550 nm) irradiation of the spiropyran coating yields a relatively hydrophobic surface (higher contact angle) that can be reversibly converted into a more hydrophilic surface (lower contact angle) with UV light irradiation. The nanowire surfaces are observed to exhibit a significant amplification in the contact angle change over that for smooth surfaces (from 12° to 23°). The roughness induced amplification of contact angle switching was accurately predicted using a Wenzel model for contact angles on fractal surfaces. These results, based on a biomimetic approach to nanotechnology, have wide ranging implications for the design of microfluidic systems.

11:20am **SS1-FrM10 Interaction of Glycine with Ice Nanolayers@footnote *@***, **G. Tzvetkov***, M.G. Ramsey, F.P. Netzer,* University of Graz, Austria

The interaction of amino acids with ice surfaces is of interest in a variety of scientific disciplines, ranging from the chemistry in interstellar space and in stratospheric clouds to processes in the geosphere and biosphere. Thin films of ice grown on crystalline substrates under ultrahigh vacuum conditions have been recognised as excellent model systems to study the surface chemistry of molecules on ice. Here we report a study of the interaction of glycine, the simplest amino acid, with ultrathin films of amorphous and polycrystalline ice, as obtained by TPD, XPS, and work function measurements. Thin ice films (@<=@50 layers) have been condensed at 110 K and at 150 K on a hydrophilic single crystalline aluminium oxide surface to produce nanolayers of low-density amorphous and polycrystalline cubic ice, respectively. Glycine overlayers have been prepared by physical vapour deposition at 110 K onto the ice surfaces and mixed glycine-ice layers by codeposition of water and glycine. Whereas the TPD of glycine at 300-350 K remains unaltered by its previous history on ice, the desorption kinetics of water in the temperature range 155-200 K is significantly influenced by the presence of glycine on the ice surfaces, with TPD peaks shifting to lower and higher temperatures with respect to those from the pristine ice surfaces. It is proposed that, on the one hand, the glycine molecules restrict the crystallisation tendency of amorphous to crystalline ice at around 140-160K, and that, on the other hand, the glycine overlayers stabilise the ice surface. The N 1s XPS spectra of the glycine molecules in the monolayer show evidence of a H-bonding interaction of the glycine amino groups with the surface O-H species. The work functions of pristine amorphous and crystalline ice surfaces and the work function changes during glycine adsorption are reported and discussed. @FootnoteText@ @footnote *@ Supported by the Austrian Science Funds.

11:40am **SS1-FrM11 H@sub 2@O-Induced Instabilities at Alumina Surfaces Under Non-UHV Conditions***, F. Qin, N.P. Magtoto,* ***J.A. Kelber,*** University of North Texas*; D.R. Jennison,* Sandia National Labs

We report that ordered, transitional phase Al@sub 2@O@sub 3@ films grown on Ni@sub 3@Al single crystal substrates undergo dramatic reorganization and morphological changes upon exposure to H@sub 2@O under non-UHV conditions at room temperature. Notably, the reconstruction does not involve the formation of an UHV-stable hydroxide. STM, AES, LEED and XPS have been used to probe the reactivities of 7 Å - 20 Å thick, ordered Al@sub 2@O@sub 3@ films grown on Ni@sub 3@Al(110) and on Ni@sub 3@Al(111) substrates for 10@super-8@ Torr < P@sub H2O@ < 1 Torr at 300 K. STM near-atomic resolution image of the surface of an as-grown Al@sub 2@O@sub 3@/Ni@sub 3@Al(110) oxide film (estimated thickness, ~ 7 Å) indicates a 10 Å repeat distance between rows, in excellent agreement with the results of a first-principles DFT calculation of an ultrathin kappa-phase film. LEED pattern of this film with a 2 x 1 unit cell confirms this structure. Both films are inert toward H@sub 2@O under UHV conditions. We demonstrate that (a) both films undergo severe surface reorganization to a rough, irregular morphology upon exposure to H@sub 2@O at pressures above 10@super-5@ Torr, 300 K, although Al(OH)@sub 3@ formation is only observed above 1 Torr, as predicted by thermodynamics and observed on sapphire(0001); (b) the film grown on the (110) substrate (Al@sub2@O@sub 3@/Ni@sub 3@Al(110)) is significantly more sensitive to H@sub 2@O vapor than the Al@sub 2@O@sub 3@/Ni@sub 3@Al(111) film, and this may be due to the incommensurate nature of the oxide/Ni@sub 3@Al(110) interface; (c) the degree of reconstruction increases with time at constant P@sub H2O@; (d) bias-dependent STM indicates that this reaction is initiated at surface terrace sites, rather than at defect sites or by diffusion to the interface; and (e) the reaction is pressure-dependent, rather than exposure-dependent, indicating that this reaction is cooperative in nature.

Surface Science
Room 210C - Session SS2-FrM

Bimetallic Surface Chemistry and Structure

Moderator: C.M. Byrd, Naval Research Laboratory

9:00am **SS2-FrM3 Tuning the Electronic and Chemical Properties of Bimetallic Surfaces***, **J.G. Chen**, J.R. Kitchin, N.A. Khan, M.A. Barteau,* University of Delaware **INVITED**

It is well known that bimetallic surfaces often show novel properties that are not present on either of the parent metal surfaces. However, it is difficult to know a priori how the chemical properties of a particular bimetallic surface will be modified relative to the parent metals. There are two critical factors that contribute to the modification of the chemical properties of a metal in a bimetallic surface. First, the geometry of the bimetallic structure is typically different from that of the parent metals, e.g. the average metal-metal bond lengths change. This gives rise to strain effects that are known to modify the electronic structure of the metal through changes in orbital overlap. Second, the presence of other metals around a metal atom also changes its electronic environment, giving rise to further modifications of its electronic structure through the ligand effect. We have investigated the electronic and chemical properties of model bimetallic surface structures, epitaxial monolayers and subsurface epitaxial monolayers, using a combination of experimental and theoretical modeling to gain further insights into these factors. In the current presentation we will first utilize the adsorption and desorption of hydrogen to demonstrate the correlation between the hydrogen binding energy and the center of the d-band in various bimetallic surfaces. We will also provide a general equation that allows one to predict how the electronic properties, especially the d-band center, will be affected in bimetallic systems. We will then use the hydrogenation of cyclohexene to demonstrate the effect of weakly-bonded hydrogen on the novel low-temperature hydrogenation activities on the bimetallic surfaces. Finally, we will use the results from the hydrogenation of cyclohexene to demonstrate a strong correlation between UHV studies on model bimetallic surfaces and reactor studies on corresponding supported bimetallic catalysts.

9:40am **SS2-FrM5 The Study of Electronic Structures and Surface Segregation of Pt@sub 3@M Alloy (M= Ti, V, Cr, Mn, Fe, Co, Ni, and Zr)***, **B.S. Mun,*** Lawrence Berkeley National Laboratory*; M. Watanabe,* Lawrence Berkeley National Laboratory & SPring-8 Project Team (RIKEN)*; V. Stamenkovic, N.M. Markovic, P.N. Ross Jr.,* Lawrence Berkeley National Laboratory

The systematic study of surface electronic structures of Pt@sub 3@M (M= Ti, V, Cr, Mn, Fe, Co, Ni, and Zr) polycrystalline alloys are presented with high resolution photoemission spectroscopy. The positions of local d-band center from valence band density of state (DOS) measurements are carefully monitored before and after annealing process. Concurrently, the presence and magnitude of surface segregation are measured with angle resolved core-level photoemission spectroscopy. The correlation between the d-band center of DOS and its chemical properties are discussed.

10:20am **SS2-FrM7 The Study of Electronic Structures and Surface Segregation of Single Crystalline Pt@sub 3@Ni(100),(100),and (111)***, **M. Watanabe**, B.S. Mun, V. Stamenkovic, N.M. Markovic, P.N. Ross Jr.,* Lawrence Berkeley National Laboratory

The surface electronic structures of Pt@sub 3@Ni(100), (110), and (111) single crystalline samples are investigated with synchrotron-based photoemission spectroscopy. From the measurement of valence band spectrum, the d-band centers of density of state are estimated and compared before and after the annealing treatment. In addition, the core-level angle resolved photoemission technique is applied to estimate the segregation of Pt and Ni at the surface. The correlation between electronic structures of each index and its chemical properties are discussed.

10:40am **SS2-FrM8 Chemisorption and Quantum Size Effects on Pseudomorphic fcc-Co and fcc-Fe Films Grown on Cu(100)***, **H. Yao**, A.G. Danese,* Rutgers University*; C.J. Bosco, F.G. Curti,* Seton Hall University*; R. Bartynski,* Rutgers University

Nanoscale metal thin films can exhibit quantum size effects (QSE) whereby their electronic, structural, magnetic and chemical properties may differ greatly from those of the bulk. The quantum confinement of electrons due to high reflectivity scattering at the film's interfaces forms so-called metallic quantum well (MQW) states which give rise to many of these interesting phenomena. In previous studies we have examined the role of MQW states in the chemisorption of CO on Cu MQW overlayers on pseudomorphic fcc-Co and fcc-Fe films grown on Cu(100). In the current work, we report on the adsorption properties of the pseudomorphic transition metal layers themselves. In addition to the fact that the pseudomorphic films represent metastable structures, these systems have partially filled d-bands that change significantly as a function of film thickness. For a Co film with an approximate coverage of 5 monolayers of Co we find that a saturation dosage of CO leads to the formation of a c(2x2) structure as observed in low energy electron diffraction. Inverse photoemission spectra of this system exhibits a two peaked structure centered at 3.8 eV above the Fermi level and is assigned to the unoccupied CO 2@pi@* orbital. CO is found to adsorb molecularly at room temperature and in TPD measurements we find a desorption temperature of approximately 400 K, a temperature in the range previously seen for CO adsorbed on hcp Co surfaces. For saturation doses carried out at lower temperatures we find a second lower temperature desorption peak around 270 K in the desorption spectra. These results, and those from fcc-Fe, are compared to the parent single crystal systems.

11:00am **SS2-FrM9 Probing the Mechanism of n-hexane Dehydrocyclization over Pt-Sn Catalysts: Adsorption and Reactivity of n-hexane, 1-hexene, and 1,5-hexadiene on Pt(111) and Sn/Pt(111) Surface Alloys***, **H. Zhao**, B.E. Koel,* University of Southern California

Supported bimetallic platinum catalysts are widely used to carry out skeletal reactions of alkanes, and such processes including dehydrocyclization are important for naphtha reforming. In order to clarify discussions of the mechanisms of these reactions, we have investigated the adsorption of n-hexane and the reactivity of several likely intermediates in such processes, i.e., 1-hexene and 1,5-hexadiene on well-defined, single-crystal surfaces of Pt(111) and two, ordered Sn/Pt(111) alloys under UHV conditions by using primarily TPD, AES, and LEED. Alloying caused a small decrease in the adsorption energy for all adsorbates. However, alloying decreased strongly the reactivity of 1-hexene and 1,5-hexadiene such that no dehydrogenation occurred during TPD on the (@sr@3*@sr@3)R30°-Sn/Pt(111) alloy with @THETA@@sub Sn@=0.33. This alloy surface does not contain pure-Pt 3-fold sites which can be inferred to be particularly reactive sites. Alloying did not decrease the saturation coverage of any of these molecules.

11:20am **SS2-FrM10 Experimental and Theoretical Characterization of the Structure of Defects at the Pyrite FeS2 (100) Surface***, **K. Andersson**, M. Nyberg,* Stockholm University, Sweden*; O. Ogasawara,* Stanford Synchrotron Radiation Laboratory*; D. Nordlund,* Stockholm University, Sweden*; T. Kendelewicz, C.S. Doyle, G.E. Brown, Jr,* Stanford University*; L.G.M. Pettersson,* Stockholm University, Sweden*; A. Nilsson,* Stanford University

Defect-free pyrite FeS2 (100) surfaces were generated and a controlled manipulation of sulfur defect density at these surfaces was performed. Sulfur species of different coordination and environments at the surface were probed by S 2p photoemission in combination with theoretical modeling of S 2p core-level shifts. A strict structural assignment of S 2p peaks at the FeS2 (100) surface in the low defect density regime was achieved. Based on our results, a defect that is related to a surface sulfur vacancy is confirmed to provide the active site for the rapid initial oxidation stage at the pyrite surface.

11:40am **SS2-FrM11 H@sub 2@S Adsorption and Dissociation on Fe-Al and Fe-Si Alloy Surfaces from First Principles***, **D.E. Jiang**, E.A. Carter,* UCLA

H@sub 2@S attacks iron aggressively and causes the formation of iron sulfide. The sulfidation process is more kinetically favorable than other processes such as carburization. We are interested in determining a way to chemically pretreat iron surfaces to improve resistance to H@sub 2@S. One strategy is to alloy the surface. Here we investigate whether alloying an Fe surface with Al or Si might improve such resistance, via periodic density functional theory calculations of H@sub 2@S adsorption and dissociation on low-index surfaces of the intermetallic compounds FeAl and Fe@sub 3@Si. Stable adsorption structures and relative stabilities of H, S, HS, and H@sub 2@S on FeAl(110), FeAl(100), Fe@sub 3@Si(110), and Fe@sub 3@Si(100) are elucidated and compared with those on Fe(110) and Fe(100). We also present predicted minimum energy paths and energy barriers for the sequential dehydrogenation steps: H@sub 2@S to HS + H and HS to H + S. Our study shows that FeAl is indeed more resistant to H@sub 2@S attack than Fe, while Fe@sub 3@Si is as susceptible as Fe.

Thin Films
Room 303C - Session TF-FrM
In-Situ/Ex-Situ & Real-Time Monitoring

Moderator: C.H. Stoessel, Consultant

8:20am **TF-FrM1 Real-time and Spectroscopic Second Harmonic Generation as a Tool to Probe Surface Processes during Amorphous Silicon Film Growth*, I.M.P. Aarts*,** *J.J.H. Gielis, C.M. Leewis, M.C.M. van de Sanden, W.M.M. Kessels,* Eindhoven University of Technology, The Netherlands

We have explored the capability of second harmonic generation (SHG) to probe surface and interface processes during the growth of amorphous silicon-based thin films such as hydrogenated amorphous silicon (a-Si:H). The a-Si:H thin films are deposited under ultrahigh vacuum conditions by means of a hot wire source on fused silica substrates. Real-time spectroscopic ellipsometry has been used to monitor the thickness evolution and the optical properties of the a-Si:H films. SHG has been observed during in situ experiments on as-deposited films for various input and output polarizations configurations. Although SHG is surface and interface specific for isotropic media such as a-Si:H, interpretation in the present case is complicated because not only interference effects have to be taken into account but also the macroscopic origin of the SHG is not straightforward to determine. The experimental data has therefore been analyzed with a complete optical model that takes into account interference effects of both the fundamental and the SHG radiation as well as two nonlinear polarizing sheets in which the SHG signal is generated. These sheets are positioned at the surface and at the interface between the film and the substrate. Further understanding of the SHG signal has been obtained by performing spectroscopic SHG measurements, which showed two distinct resonance peaks at photon energies of 1.2 and 1.4 eV. After exposing the a-Si:H film to oxygen the SHG signal is quenched, indicating that the corresponding resonance peaks involve transitions with dangling bond states. In addition, real-time observation of the SHG signal during film growth and dosing experiments have already revealed that SHG is sensitive to nucleation and relaxation processes at the surface and/or interface region during and after growth of these silicon-based films.

8:40am **TF-FrM2 MultiChannel Mueller Matrix Ellipsometry for In-Situ and Real Time Analysis of Thin Films and Surfaces*, R.W. Collins*,** *C. Chen, I. An, N.J. Podraza,* University of Toledo **INVITED**

A dual rotating compensator multichannel ellipsometer has been applied for real time Mueller matrix spectroscopy (2 to 5 eV) of anisotropic surfaces and thin films. The sequence of optical elements for this instrument is denoted PC@sub 1@SC@sub 2@A, where P, S, and A represent the polarizer, sample, and analyzer. C@sub 1@ and C@sub 2@ represent the first and second compensators that rotate at frequencies of 10 and 6 Hz, respectively, synchronized for a 5:3 ratio. At this ratio, the 2n@omega@ frequencies where n = 1, ..., 8, 10, 11, 13, and 16, and where @omega@/2@pi@ = 2 Hz, are present in the detected irradiance waveform for the most general sample Mueller matrix. The associated 25 experimental dc, cosine, and sine Fourier coefficients are determined for a given pixel of the photodiode array detector by integrating the waveform 36 times per optical cycle. Spectra in the 16 Mueller matrix elements can be determined from spectra in the 25 non-zero coefficients acquired in a single 250 ms optical cycle and from instrument calibration data obtained in advance. In high speed Mueller matrix measurements, this research has focused on weakly anisotropic surfaces and thin films that push the instrument to its limits. These include the (110) Si surface and thin films having an oriented columnar microstructure in which case the weak anisotropic optical response can be over-determined from analyses employing separate 2x2 blocks of the Mueller matrix. As a result, detection of anisotropy is definitive, and the co- and cross-polarization ellipsometric angles @psi@@sub pp@, @psi@@sub ps@, and @psi@@sub sp@ can be determined to within an accuracy of 1 part in 10@super 4@.

9:20am **TF-FrM4 Analysis of Ti and TiN Thin Film Nucleation, Coalescence, and Growth by Rotating Compensator Multichannel Ellipsometry*, C. Chen*,** The Penn State University*; B. Hong,* Sungkyunkwan University, Korea*; P. Sunal, M.W. Horn, R. Messier,* The Penn State University*; R.W. Collins,* University of Toledo

Real time spectroscopic ellipsometry has been applied in the rotating-compensator configuration to characterize the nucleation, growth, and optical properties of titanium and titanium nitride thin films deposited by magnetron sputtering on silicon wafers with thermally-grown silicon oxide and nitride overlayers. The ellipsometer used in this study incorporates recent instrumentation advances for a wide spectral range (1.5 to 6.5 eV), including a dual Xe/D@sub 2@ source with an intervening iris for spectral flattening. The real time ellipsometric spectra collected throughout film deposition on the smooth wafer substrates are analyzed in terms of a transition from a one-layer to a two-layer optical model. This transition simulates the overall thin film structural evolution including nucleation, coalescence, and surface roughening during growth. In the initial stages, the spectra are particularly sensitive to smoothening that occurs during coalescence. In the case of Ti deposition on SiO@sub 2@ covered Si wafers, for example, this effect is maximized within a narrow deposition parameter window of Ar sputtering gas pressure and plasma power. In this case, 15-20 Å thick Ti clusters coalesce, yielding surface roughness only a monolayer in thickness after ~100 Å of Ti bulk layer deposition. The evolution of the optical properties of the Ti layer with cluster size during nucleation and with bulk thickness during growth provides additional information on the structure of the film and its electronic properties. Finally, insights from these studies can be used to direct the fabrication of alternating multilayer and nanocomposite films for hard-coating applications.

9:40am **TF-FrM5 Comparative Ellipsometric Study of Liquid Helium Thin Films on Au, Cs, HOPG and Rb Substrates*, T. McMillan*,** *P. Taborek, J.E. Rutledge,* University California Irvine

We have developed a modulated null ellipsometer with sub-monolayer resolution to measure adsorbed liquid helium thin films at temperatures from 1.3 to 4.3 K. Measuring helium films pushes the limits of cryogenic ellipsometry due to helium's extremely small index of refraction. We have performed isotherms on substrates with a range of substrate potentials: Au is a representative strong substrate while Rb is an intermediate and Cs a weak substrate. These measurements will determine how the binding energy affects the superfluid transition. The ellipsometer allows us to explore effects that cannot be discerned solely from quartz crystal microbalance measurements, which are only sensitive to the normal fluid fraction of the film.

10:00am **TF-FrM6 Studies of Coupling and Ordering in Magnetic Thin Films with Polarized Neutron Reflectormetry*, S.G.E. te Velthuis*,** Argonne National Laboratory **INVITED**

Traditionally neutron scattering has been an important tool for studying bulk magnetic materials. The success has been due to the high sensitivity of neutrons for magnetic moments, combined with their characteristics in relationship to wavelength and velocity. As the interest of the scientific community has shifted towards nanostructured materials, polarized neutron reflectivity (PNR) and scattering at grazing incidence have emerged as powerful methods for studying magnetic thin films. As will be illustrated by the presentation of several experiments, the depth dependent magnitude and orientation of the magnetization in a thin film can be determined with PNR. In the case of GaMnAs thin films knowledge about the magnitude of the magnetization provided understanding about the effect of temperature annealing in these films. Determination of the orientation of the magnetization of individual Fe layers in Fe/Cr[110] superlattices as was essential to the understanding of the magnetic coupling between the Fe layers spaced by Cr. Finally, PNR experiments performed with polarization analysis mapped out the evolution of individual magnetization vectors during the first order spin flop transition in a finite antiferromagnet, thereby confirming theoretical predictions about this magnetic phase transition.

10:40am **TF-FrM8 Real-time Optical Monitoring of Ammonia Decomposition Kinetics in InN Vapor Phase Epitaxy at Elevated Pressures*, N. Dietz*,** *M. Strassburg, V. Woods,* Georgia State University

Understanding the decomposition kinetics of the chemical precursors involved in nucleation and thin film growth processes is crucial for controlling the growth process. The growth of emerging materials heterostructures such as InN and related alloys requires deposition methods operating at elevated vapor densities due to the high thermal decomposition pressure in these materials. High nitrogen pressure has been demonstrated to suppress thermal decomposition of InN, but has so far not been explored in chemical vapor deposition experiments. The extension of chemical vapor deposition (CVD) to elevated pressure opens an avenue for retaining stoichiometric single phase surface composition for materials that are characterized by large thermal decomposition pressures at optimum processing temperatures. In this contribution we present research results on the decomposition kinetics of ammonia in the laminar flow regime of a high-pressure flow channel reactor. Real-time optical UV absorption and fluorescence spectroscopy has been applied to study the gas phase chemistry as function of flow, pressure and temperature. Data are presented for the optical methods of real-time process monitoring to analyze the decomposition process as well as the initial stages of InN heteroepitaxy.

11:00am **TF-FrM9 In-Situ Real-Time FT-IR Spectroscopy During APCVD: The Effect of B and P Dopants on SiO@sub 2@ Deposition***, A. Effenberger, L.D. Flores,* ***J.E. Crowell,*** University of California, San Diego

In-situ FT-IR spectroscopy has been used to explore the chemical boundary layer (CBL) region formed during atmospheric pressure chemical vapor deposition. Infrared spectra are recorded in 22 second intervals while varying the precursor gas composition. Using TEOS and ozone precursors in combination with borates and/or phosphites, thin films of boro-, phospho-, or borophosphosilicate glass are deposited onto Si wafers at 725K. Gas phase intermediates containing SiOH and BOH functionalities have been observed, and their variation with chemical composition has been investigated. A partial least squares principle component analysis has been used to quantify the reactive chemical mixtures and to evaluate the effect of dopants on the chemical kinetics.

11:20am **TF-FrM10 Optimal Control on Composition and Optical Properties of Silicon Oxynitride Thin Films***,* ***E.C. Samano****, J. Camacho, R. Machorro,* CCMC-UNAM, Mexico

The desire to merge the most advantageous physical and chemical properties of both SiO@sub 2@ and Si@sub 3@N@sub 4@ in an optimum combination tailored to various applications in electrical, optical and optoelectronic thin films has pushed a continuous interest in the processing of SiO@sub x@N@sub y@ thin films. Inhomogeneous thin film filters have had an increasing importance in the industry as optical filters. Silicon oxynitride, SiO@sub x@N@sub y@, is a very interesting material for multiple applications, including graded refractive index films. The refractive index can be changed from pure silicon dioxide (1.47) to silicon nitride (2.4) by just varying the film composition. We report the growth of SiO@sub x@N@sub y@ films by reactive laser ablation using two different solid targets, Si@sub 3@N@sub 4@ and Si, in the ambient of N@sub 2@ and O@sub 2@ at various pressures, introduced separately in the growth chamber, as the film is monitored by real time ellipsometry. The oxidation rate in the films is studied for both targets. The composition of the films is in situ determined by AES and XPS. The evolution of the chemical bonding of the species in the film is done by FTIR. The SiO@sub x@N@sub y@ film stoichiometry, bonding character and optical properties are compared as a function of O@sub 2@ pressure while N@sub 2@ pressure is maintained fixed as either the Si@sub 3@N@sub 4@ or Si target is ablated.

11:40am **TF-FrM11 III Nitride-Based Optical Sensors Integrated with a TOF Mass Spectrometer for Aerosol Characterization.***, D. Starikov, N. Medelci, R. Pillai,* Integrated Micro Sensors Inc.*; A. Bensaoula,* ***C. Joseph****, Z. Mouffak,* University of Houston

Mass spectrometry is currently an essential aerosol characterization tool. For many important biochemical and biomedical applications it would be beneficial to perform optical characterization of the aerosol prior to mass spectrometry. Such characterization would include particle detection, evaluation of the particle size, shape, velocity, etc. Rugged multifunctional multi-wavelength solid-state optical sensors fabricated from III nitride based components have a miniature size and demonstrated high performance in detecting various important compounds. In this work integration of our miniature solid-state optical sensors based on III nitrides with a compact Time-of-Flight (TOF) mass spectrometer has been attempted. The sensors were tested ex situ by fluorescence, absorption, and scattering measurements performed on solutions of fluorescein, rhodamine, erythrosine, chlorophyll, pyrene, anthracene, alexa fluor, and red fluorescing microsphere fluorochromes. These measurements indicated that some of the compounds can be detected with a sensitivity as low as 4-5 ppm in a wide range of concentrations. After integration with an ORTOF mass spectrometer (Ionwerks Inc.), the sensors will be tested for detection and characterization of fluorescing and non-fluorescing aerosols. The sensitivity, dynamic, range, detection limits will be evaluated for various aerosol analytes.

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