Monday Morning, October 2, 2000

Biomaterial Interfaces
Room 202 - Session BI+SS-MoM

Biological Surface Science

Moderator: D.G. Castner, University of Washington

8:20am **BI+SS-MoM1 Suspended Lipid Bilayers on Porous Alumina Surfaces***, **C. Steinem**, J. Drexler, C. Hennesthal,* WWU Muenster, Germany

The study presents a new class of artificial membrane system "suspended bilayers" closing up the gap between solid supported membranes (SSMs) and black lipid membranes (BLMs). Suspended bilayers were prepared on the basis of porous alumina surfaces which were produced by an anodic etch of neat alumina foils. Gold was evaporated on the upper surface of the porous material. The porous material was characterized by scanning electron microscopy (SEM), scanning force microscopy (SFM) and impedance spectroscopy. As revealed by SEM and SFM pores exhibit a mean diameter of 65 nm. Functionalization of the upper gold surface was achieved by self assembly of 3-mercaptopropionic acid (MPA) rendering the surface negatively charged at pH 8.6. To obtain suspended solid supported we fused unilamellar vesicles of N,N-dimethyl-N,N-dioctadecyl ammonium bromide varying in their sizes on the MPA-covered surface. Bilayer patches spanning the pores were visualized by scanning force microscopy in buffer using contact mode. The bilayer covered nanopores are thought to serve as second aqueous compartments of femtoliter volume providing enough space to incorporate transmembrane proteins and to generate ion gradients across the membrane together with the ability to use sensitive surface analysis tools.

8:40am **BI+SS-MoM2 Formation and Characterization of Stabilized Supported Phospholipid Bilayers***, **S. Saavedra**, E. Ross, J. Conboy, S. Liu, D.F. O'Brien,* University of Arizona

The utility of phospholipid bilayers as non-fouling coatings in molecular device technologies is hampered by the chemical and mechanical instability of these structures relative to (for example) alkylsiloxane self-assembled monolayers. Towards the use of lipid bilayers in applications such as biosensing, we have investigated two-dimensional polymerization as a strategy to stabilize planar supported lipid bilayers. UV-induced and redox-initiated polymerization have been used to prepare air-stable bilayers from phosphatidylcholine monomers containing sorbyl moieties in the acyl chains. Preparation of these structures using Langmuir-Blodgett-Kuhn and vesicle fusion techniques, and characterization of their physical and chemical properties, including nonspecific protein adsorption behavior, will be described.

9:00am **BI+SS-MoM3 Regulating Molecular Recognition and Self-assembly via Mechanical Forces: The Cell Adhesion Protein Fibronectin at Phospholipid Interfaces***, A. Krammer, G. Baneyx, D. Craig,* University of Washington*; K. Schulten,* University of Illinois at Urbana-Champaign*;* ***V. Vogel,*** University of Washington **INVITED**

While major progress has been made in the past to reveal how chemical factors regulate biorecognition, insight into pathways by which nature utilizes external forces to regulate biorecognition and signaling holds the potential for major new discoveries in biomedicine. Knowledge in this field is rudimentary since high-resolution crystallographic structures of biomolecules have mainly been obtained from equilibrated states. The role played by mechanical forces applied to the terminal ends of domains in regulating exposure of their recognition sites will be discussed here for the multidomain protein fibronectin. One of fibronectins many functions is to promote cell adhesion to surfaces. Starting from the equilibrium structure of fibronectin type III domains (FnIII), steered molecular dynamics simulations were applied to study the pathway by which their tertiary structures unravel under external forces. First we found that the accessibility of the cell recognition site on the FnIII10 domain, i.e. the RGD-loop, to integrins is reduced in an early stage of the forced unfolding pathway. Furthermore, forced unfolding studies of various fibronectin type III modules have shown that FnIII-7, FnIII-8, FnIII-9 and FnIII-10 differ considerably in their mechanical stability, and the simulations predict that FnIII-10 unfolds first. Finally, we have experimentally analyzed the pathway on which fibronectin assembles into fibrillar networks underneath phospholipid monolayers, and find again that mechanical forces are crucial to initiate its spontaneous self-assembly. Thus, spontaneous assembly of fibronectin into fibrils cannot be induced by adsorption to solid surfaces, yet it is the fibrillar state that allows cells to apply the forces needed to partially unfold fibronectin's domains.

9:40am **BI+SS-MoM5 New Methods for Patterning Fluid Lipid Bilayer Membranes on Solid Supports***, **J.S. Hovis**, S.G. Boxer,* Stanford University

Two new methods are introduced for patterning fluid lipid bilayer membranes on solid supports. These methods, called blotting and stamping, rely on the observation that supported lipid bilayers exhibit self-limiting lateral expansion. The consequence is that it is possible to pattern these fluid surfaces without modifying the underlying substrate. Together these methods constitute a simple and powerful approach for preparing patterned fluid lipid bilayers in nearly any geometry. One important application of these methods is the ability to create composition arrays of lipids and membrane associated proteins. These arrays allow the opportunity to study lipid-lipid, lipid-protein, and/or protein-protein interactions in a parallel fashion. Information gained about these important biological interactions will be highlighted.

10:00am **BI+SS-MoM6 The Interaction of Phospholipid Vesicles with Binary Alkanethiol/Hydroxythiol Monolayers***, **V. Silin**,* National Institute of Standards and Technology*; H. Wieder,* Max Planck Institute for Polymer Research, Germany*; J. Woodward, A. Plant,* National Institute of Standards and Technology

Surfaces modified by self-assembly have applications in sensors, diagnostics, chemical processing, and biomaterials, where they may incorporate features such as molecular recognition and enzymatic activity. Understanding the forces that direct self-assembly of biologically important molecules in predictable arrangements will aid the development of such applications. The focus of this study is a mimic of biological membranes formed by the interaction between two self-assembled systems: phospholipid amphiphiles that associate into bilayer vesicles in water, and monolayers of alkanethiols on metal surfaces. We have studied the interaction of small (60nm) POPC vesicles with binary thiol monolayers of known surface free energy. The surfaces were prepared on gold by self-assembly from binary solutions of the thiols CH3-(CH2)10-X (X = CH3; OH) in THF. The surface plasmon resonance (SPR) technique was utilized to follow the vesicle fusion kinetics and to characterize the resulting assemblies. A dramatic influence of the surface layer composition on the formation of POPC films was observed. The formation of an additonal POPC monolayer was detected only on the completely hydrophobic (100% CH3) surface. The largest thickness of POPC layer was detected at a CH3/ OH ratio of 50% (in the assembly solution). For the completely hydrophilic surface (100 % OH) the POPC layer thickness was found to be close to the thickness of a phospholipid bilayer. Thus, the increase of hydrophilic component on the surface leads to the formation of an unordered POPC film that seems to contain a mix of fused and unfused vesicles. Most likely the formation of an ordered bilayer of POPC molecules has been observed for the completely hydrophilic surface. The SPR data were supported by AFM, capacitance and contact angle measurements.

10:20am **BI+SS-MoM7 Formation of 2D Crystals of Proteins on Solid Supports, and Their Application for Immobilizing Molecules or Particles***,* ***A.D.R. Brisson,*** University of Groningen, The Netherlands **INVITED**

The immobilization of molecules or particles on solid supports constitutes a central issue in various fields, eg. the immobilization of enzymes in the biosensor area, or the immobilization of DNA molecules on microarrays in genomics. Existing technologies rely mainly on the chemical modification of solid surfaces and the subsequent immobilization of the molecules of interest via non-specific interactions. The strategy we have selected is based on the use of functionalized 2D crystals of proteins formed on solid-supported lipid bilayers (SPBs) as a matrix for anchoring proteins/particles in a specific manner. Its main potential advantages are the wide panoply of functional groups that could be introduced in proteins, the well-known chemistry of the coupling reactions involved, the well-defined density of anchoring groups, and the specificity of the coupling reactions ensuring an oriented binding of bound molecules. In addition, protein 2D crystals could serve as templates for creating ordered arrays of immobilized particles, at the nanometer scale. The formation of SPBs by fusion of lipid vesicles on mica,@footnote 1@ and the growth of protein 2D crystals on SPBs were extensively studied by AFM and Electron Microscopy (EM) in the case of two protein systems, annexin V@footnote 2@ and streptavidin. Pre-formed 2D arrays of modified annexin molecules were used for immobilizing proteins, liposomes, and membrane fragments containing membrane proteins. An unexpected result was the induced ordering of membrane proteins resulting from their specific binding to an ordered protein matrix. On the other hand, while close-packed assemblies of liposomes could be bound to protein 2D arrays, attempts to fuse them into suspended lipid bilayers have yet been unsuccessful. The immobilization of inorganic particles is under investigation. Results of these studies will be presented. @FootnoteText@@footnote 1@Reviakine et al. Langmuir 16, 2000, 1806. @footnote 2@Reviakine et al. J. Struct. Biol. 121, 1998, 356.

Material Characterization
Room 207 - Session MC-MoM

Depth Profiling

Moderator: F.A. Stevie, Lucent Technologies

8:20am **MC-MoM1 Valence Model Based Correction of Ultra Shallow Depth Profiles***, **O. Brox**,* University of Muenster, Germany*; D. Gehre, E. Zschech,* AMD Saxony Manufacturing GmbH, Germany*; A. Benninghoven,* University of Muenster, Germany

In recent years lateral and in-depth dimensions of microelectronic devices have shrunk by orders of magnitude. The reduction in depth scale was supported by the application of ultra low implantation energies of dopant materials. As a consequence a significant part of the implanted species is located in the uppermost monolayers. The entire thickness of the shallow implants used nowadays of less than 10 nm implanted in oxides with a thickness up to 3 nm complicates the establishment of quantitative SIMS depth profiles. Changing conditions regarding the oxidation state require corrections of the concentration- and depth scale. Distortions can occur also due to the very high peak concentrations (distinctly higher than 1%) resulting from the ultra low implantation energies and from contamination layers as hydrocarbons e.g. For all experiments we used TOF instruments, equipped with flexible gas ion sources and cesium sources (0.6 - 10 keV) for crater formation. Additional gas ion sources (Ar@super +@, 11 keV) have been applied for the analysis of the crater bottom. We have investigated the possibility to compensate the falsification caused by changes of the secondary ion yield in the transient region by applying a suitable correction procedure based on the so-called lattice valency model.@footnote 1@ The success of this correction will be demonstrated by a quantitative depth profile of a 10 keV As-implant into a 3 nm screening oxide. The sputter behavior of undefined organic contaminations as well as of well defined polymer overlayers has been investigated. Sputter yields, damage cross sections, and thermal desorption behaviors will be reported. They allow an estimation of possible depth scale distortions. . @FootnoteText@ @footnote 1@ C. Plog, L. Wiedmann, A. Benninghoven, Surf. Sci. 67 (1977) 565.

8:40am **MC-MoM2 Analysis of Ultra-thin Oxynitride Layers by TOF-SIMS***, **E. Niehuis**, T. Grehl, R. Möllers,* ION-TOF GmbH, Germany*; O. Brox,* University of Münster, Germany

The analysis of very thin oxynitride layers with a thickness below 3 nm becomes increasingly important. Methods are needed to determine the layer thickness, the nitrogen content and the nitrogen distribution in a quantitative manner. The film thickness can be measured with high reproducibility by Ellipsometry, but the SiO@sub 2@/Si interface properties and contamination layers can influence the accuracy. The total N content for very thin films can be quantified using XPS. However, no analytical technique can give the quantitative N distribution with sufficiently high depth resolution and sensitivity. SIMS depth profiling using Cs primary ions in the energy range of 500-1000 eV has been used extensively to study oxynitrides. However, the transient width in this energy range is still above 3 nm. In order to reduce it below the thickness of the film, very low energies of 100-300 eV and/or high impact angles are required. The low sputter yield in this energy regime leads to extremely high Cs surface concentration and to significant sputter rate changes in the transient regime. We have investigated the capabilities of Cs depth profiling at very low energies using TOF-SIMS depth profiling in the dual beam mode. A Cs beam with an energy below 300 eV has been used for the erosion while the center of the sputter crater is analysed with a high energy Ga beam. We have used a new Cs-Xe co-sputtering method to control the Cs surface concentration and keep it in the optimum range for the formation of MCs@super +@ cluster ions. The achievable depth resolution, the sensitivity for nitrogen and the accuracy of the thickness measurement will be discussed in detail.

9:00am **MC-MoM3 Ion Beam Studies of Ultrathin Metal Oxide Dielectrics***, **E. Garfunkel**, B. Busch, H. Schulte, T. Gustafsson,* Rutgers University**INVITED**

There is a strong need to find silicon-compatible high dielectric constant (high-K) replacements for silicon dioxide in microelectronics. This presentation describes recent results on the structure, composition, growth and annealing behavior of high-K combinations of Zr, Hf, Y, and La oxide films. Results will be presented from ion scattering, scanning probe microscopy, photoelectron spectroscopy, electron microscopy and several other surface and thin film methods. It is found that only by cross-correlating several different methods can a definitive analysis of structure and composition (including the depth profile) be given. The interaction of isotopically labeled oxygen with ultrathin oxides at elevated temperatures shows oxygen exchange and diffusion in the films, as well as deleterious silicon dioxide interface growth (that unfortunately accompanies many post-growth anneals). Problems associated with crystallization, interdiffusion, electrical breakdown, and interface structure will also be addressed.

9:40am **MC-MoM5 Matching the High Dose Ultra Shallow As Doping Profiles Measured by X-ray Photoelectron Spectroscopy, Magnetic Sector Secondary Ion Mass Spectrometry and Low Energy Quadrupole Secondary Ion Mass Spectrometry***, J. Zhao, C.M. Jones, **T. Neil**,* Advanced Micro Devices*; D. Zhou,* University of Central Florida

SIMS has proven to be a powerful technique for dopant depth profile analysis, however, quantification of dopant concentrations in the outermost several nanometers is still not at all trivial. A major problem arises because SIMS analysis exhibits a surface transient before reaching equilibrium in the sputtering process. Ion yields and sputtering-rate vary significantly during the transient zone and after reaching the equilibrium. The surface transient can be reduced to a few nanometers if a low-energy primary ion beam is used, but a further reduction is hindered by the presence of native oxide of varying thickness on Si wafers. For ultra-shallow As doping profiles using Cs@super +@ primary ions, which increases the negative secondary ion yields, surface oxide significantly depress the As@super ?@ negative ion yield. In the present work, an attempt of using XPS depth profiling to determine the high dose ultra-shallow As dopant profile, with particular interests in the dopant distribution and concentration within the surface transient region, was reported. XPS quantification is free from the ion yield and erosion rate variations of SIMS quantification, and a detection limit of 3e19at/cm@super 3@ for As is demonstrated. XPS results show higher As concentration up to ten times at the sample surface region (<10nm) than that of magnetic sector SIMS result. In addition, the feature of As piled up at the interface of surface oxide and Si substrate was clearly detected in the XPS depth profile, but missed in the magnetic sector SIMS depth profile. After the first 10nm, XPS and magnetic sector SIMS depth profiles match each other, and magnetic sector SIMS demonstrates a superior detection limit down to 5e16at/cm@super 3@. A comparison of the As dopant profiles measured by low energy quadrupole SIMS and magnetic sector SIMS, which was corrected by XPS for the surface transient region, will be further discussed in the paper.

10:00am **MC-MoM6 XPS Characterization of NO Oxynitride Films using Chemical Profiling***, **I.S. Choi**, H.J. Kim, S.Y. Lee,* Hyundai Electronics Industries Co., Ltd., Korea

For the fabrication of MOS devices, the incorporation of nitrogen into thin SiO2 dielectric films has been shown to improve the electrical and structural property of the films. Some benefits of these oxynitrides are as following: (a) resistance to boron diffusion, (b) immunity to hot carrier effects, (c) higher charge-to-breakdown voltage, and (d) reduced charge trapping. These improvements are owing to accumulation of nitrogen atoms at the dielectric/silicon interface. The depth profile and chemical environment of nitrogen in oxynitride films is a critical information to the process control so that a lot of technique to study this material have long been used.@footnote 1,2,3@ However, Ar ion sputtering usually used to acquire depth profile may affect the actual concentration and the bond characteristic of N. In this X-ray photoelectron spectroscopic study of oxynitride films, we adopted successive delicate etching of the films with dilute HF solution as a technique for profiling. It was believed that this kind of chemical profiling would not affect the actual concentration and chemical environment of the films. The etch step was finely controlled to have etch rate of ~0.5 ¢®?/sec and the thickness of every slicely etched films were measured by XPS. With the help of this chemical profiling technique, we observed, for the first time, the selectivity of the etch rate between the thermal oxide and oxynitride films. Much difference between the etch rate of two films was used to remove upper oxide layer and study remained pure oxynitride film. Therefore we could directly observe the thickness of NO oxynitride interlayer to be about 6¢®?.@footnote 4@ We also have studied the bond structure, thickness, and composition of the oxynitride layers by deconvoluting Si2p and N1s XPS spectra. The results of the study on the composition and the chemical environment of the oxynitride films will be discussed in this presentation. @FootnoteText@

@footnote 1@ Rama I.Hegde, Philip J. Tobin, Kimberly G. Reid, Bikas Maiti, and Sergio A. Ajuria, Appl. Phys. Lett. 66(21), 2882 (1995) @footnote 2@ E. P. Gusev, H. C. Lu, T. Gustafsson, E. Garfunkel, M. L. Green, and D.Brasen, J. Appl. Phys. 82(2), 896 (1997) @footnote 3@ M. R. Frost, C. W. Magee. Appl. Surf. Sci. 104/105, 379 (1996) @footnote 4@ E. A. Irene, Q. Liu, W. M. Paulson, P. J. Tobin, and R. I. Hegde, J. Vac. Sci. Technol., B14, 1697 (1996)

10:20am **MC-MoM7 The Effect of Ion Acceleration Voltage on Interface Resolution During Depth Profiling and the Application of Advanced Data Analysis Techniques***, **S.J. Hutton,*** Kratos Analytical, UK*; N. Fairley,* CASAXPS Ltd, UK*; D. Surman,* Kratos Analytical, UK

The effect of ion acceleration voltage on interface resolution during destructive depth profiling of a challenging multilayer sample was investigated. A compact, high speed, Kaufman ion source combined with X-ray photoelectron spectroscopy (XPS) enabled efficient concentration depth profiling through several hundred nanometer thick layers. The Kaufman source exhibits extremely high sputter rates at low ion beam acceleration potentials reducing ion induced mixing of the surface atoms. Atomic concentration profiles through inorganic oxide layers were recorded as a function of ion acceleration voltage. The improvement in interface resolution with decreasing acceleration voltage was clearly demonstrated. Chemical state information was retained with some reduction of the oxide layer observed due to preferential sputtering of oxygen from the surface during profiling. A detailed examination of the O 1s envelopes was also performed using principal component analysis (PCA) and non-linear least-square curve fitting (NLLSCF). It was shown that while four abstract factors characterised the O 1s data only two were of chemical significance with the remaining pair describing trends associated with the measurement process. Sub-sampling the periodic nature of the data matrix allowed underlaying line-shapes to be identified which were used to support the NLLSCF data reduction.

10:40am **MC-MoM8 Quantitative Comparison between AES and SIMS Depth Profiles of a Double Layer Structure of AlAs in GaAs Using the MRI-model***, **S. Hofmann,*** Max-Planck-Institute for Metals Research, Germany*; A. Rar,* University of Alabama*; D.W. Moon,* Korea Research Institute of Standards and Science, Korea*; K. Yoshihara,* National Research Institute for Metals, Japan

Application of the so called mxing-roughness-information depth (MRI)-model@footnote 1@ to the quantitative reconstruction of the in-depth distribution of composition, is demonstrated by a comparison of SIMS and AES depth profiles. A GaAs/AlAs reference sample consisting of two layers of AlAs (1 ML and 36 ML) separated by 44 ML of a GaAs matrix was depth profiled using almost identical sputtering conditions: Ar+ ions of 3 keV impact energy and 52 (SIMS: CAMECA 4f) and 58 deg. (AES: VG Microlab 310F) incidence angles. Both the Al+ intensity of the SIMS profile and the Al (LVV) intensity of the AES profile were quantified by fitting the measured profiles with those calculated with the MRI model, resulting in the same mixing length of 3.0 nm ± 0.3 nm, similar roughness parameter (1.4-2 nm), and negligibly small information depth (0.4 nm)for SIMS. Whereas practically no matrix effect was observed for Al+ in the SIMS profile, quantification using dimer ions (Al2+) shows a marked nonlinearity between concentration and intensity.@footnote 2@ @FootnoteText@@footnote 1@S. Hofmann, Surf. Interface Anal. 27,(1999)825. @footnote 2@A. Rar, D.W. Moon and S. Hofmann, J. Surf. Anal. 6,(1999)29.

Magnetic Interfaces and Nanostructures
Room 206 - Session MI-MoM

Magnetic Spectroscopies

Moderator: S.D. Bader, Argonne National Laboratory

8:20am **MI-MoM1 Spin Polarized Photoemission Study of Magnetite Films: Extraction of the Bulk Polarization via a Substrate Overlayer Model***, **S.A. Morton,** G.D. Waddill,* University of Missouri, Rolla*; J.G. Tobin,* Lawrence Livermore National Laboratory*; S. Kim, I.K. Schuller,* University of California, San Diego*; S.A. Chambers,* Pacific Northwest National Laboratory

Many materials have been predicted to be half metallic, yet to date remarkably little truly compelling evidence for this behavior has emerged. One technique that can potentially yield a definitive result is spin polarized photoemission and it is from this technique that the most compelling evidence yet has emerged.@footnote 1@ However such experiments are hampered by the difficulty in producing clean stoichiometric surfaces with a polarisiation that is truly representative of that of the bulk. We have used the spin-resolved photoemission facility at the Advanced Light Source,@footnote 2@ to study the half-metallic candidate Fe@sub 3@O@sub 4@, which holds out the possibility of use in spintronic devices as a pure spin source. The epitaxial films were grown on MgO by UCD and PNNL and were characterized by RHEED, LEED, XRD, and magneto-transport measurements. We have demonstrated that cleaning the samples results in the loss of their polarization. However, our ability to perform spin resolved experiments at higher photon energies, (as a direct result of the high brightness of the 3rd generation source), has enabled us to study the near Fermi edge polarization of the samples "as received", without having to resort further to potentially destructive cleaning techniques. By measuring the polarization as a function of emission angle and photon energy, and combining these measurements with a substrate overlayer model, we have been able to extract the underlying polarization of the bulk material and have demonstrated that it is significantly higher than the 30% initially observed in the "as-received" samples, and may indeed be up to 100%. Furthermore, our spin resolved spectra demonstrate close agreement with simulated spectra derived from theoretical calculations.@footnote 3@ @FootnoteText@ @footnote 1@Park et al, Nature 392 794 (1998); Phys. Rev. Lett. 81 1953 (1998)@footnote 2@Tobin et al, MRS Symp. Proc. 524 185 (1998)@footnote 3@Zhang and Satpathy, Phys. Rev. B. 44 13319 (1991).

8:40am **MI-MoM2 Magnetic Dichroism in the Soft X ray Absorption Region of NiMnSb Ferromagnetic Alloy***, **C.N. Borca,*** University of Nebraska, Lincoln*; S. Stadler,* Naval Research Laboratory*; D. Ristoiu,* CNRS Laboratoire Louis Neel, France*; P.A. Dowben,* University of Nebraska, Lincoln*; Y.U. Idzerda,* Naval Research Laboratory*; J.P. Nozieres,* CNRS Laboratoire Louis Neel, France

We have investigated the magnetic and electronic structure of NiMnSb alloy by soft-X-ray absorption spectroscopy (XAS) and magnetic circular dichroism (MCD) measurements in the Mn 2p and Ni 2p core absorption regions. We have studied the unoccupied orbital symmetry of NiMnSb. The spectra display strong polarization dependence, especially at the Mn 2p threshold. The unoccupied orbital assignment will be presented as a function of temperature and light polarization. The apparent multiplet structures found in the Mn 2p XAS spectra corresponds to a tetragonal crystal field symmetry and is the origin of most of the moment in this Heusler alloy. The XAS spectrum in the Ni 2p core shows a doublet feature in both 2p3/2 and 2p1/2, resulting from the octahedral crystal field.

9:00am **MI-MoM3 Cu Metallic Quantum Well State Dispersions in the Cu/fccFe/Cu(100) System***, **A. Danese,** R.A. Bartynski,* Rutgers University

Multilayers of alternating ultrathin non-magnetic/ferromagnetic (NM/FM) films often exhibit oscillatory magnetic coupling between sequential FM layers. This phenomenon has great technological importance and is associated with the presence of metallic quantum well (MQW) states in the NM layer. To understand the influence of the FM substrate on the electronic states of the NM layer, we have performed an inverse photoemission (IPE) study of the Cu/fccFe/Cu(100) system along the @Gamma@X direction of the surface Brillouin zone (SBZ). We have also modeled this system using a phase accumulation approach. The model predicts that a subset of these states disperse slowly as a function of parallel momentum in the region of the projected spin polarized band gap of the FM layer, which for fccFe lies a few eV above the Fermi energy. We will discuss IPE results for Cu/fccFe/Cu(100) system in this region of the SBZ, both above and below the Curie temperature of the Fe layer. We have also investigated thermal desorption of CO from this system as a function of Cu film thickness to determine how the presence of MQW states influences the chemisorption bond.@footnote 1@ @FootnoteText@ @footnote 1@Supported by NSF-DMR #98-01681 and ACS-PRF #33750-AC6,5.

9:20am **MI-MoM4 On the Evolution of Magnetic Moments of Fe in FeCo(100) & FeNi(100) Alloy Films***, **N.A.R. Gilman,** R. Zhang, R.F. Willis,* Pennsylvania State University*; M. Hochstrasser, J.G. Tobin,* Lawrence Livermore National Laboratory

We report on the variation of the local magnetic moments with changing composition in Fe@sub x@Co@sub 1-x@ and Fe@sub x@Ni@sub 1-x@ alloy films grown epitaxially on fcc Cu(100). The elemental magnetic moments were determined from magnetic-field-induced intensity asymmetry observed in angle-dependent photoelectron spectroscopy of the 3p core-levels of the constituent atoms - "x-ray magnetic dichroism.@footnote 1@ Both the Fe and the Ni moments change in magnitude with changing composition of FeNi alloys.@footnote 2@ The 'stoichiometrically averaged moment' follows the Slater-Pauling curve up to a critical filling of the 3d bands (corresponding to ~2.5 holes in the minority-spin d-band) at which point it collapses to a lower spin-state ('Invar' effect). This is caused by a sudden change in the Fe local moment. This magnetic instability is predicted theoretically independent of what element the Fe is alloyed with ie, a similar collapse is expected for FeCo alloys at the same critical filling of the d-bands.@footnote 3@ However, to date, no such collapse of the Fe moment has been observed in similarly grown FeCo alloy films with fcc-like pseudomorphic structure. In this paper, we present new results comparing the evolution of the Fe moments in FeNi and FeCo fcc pseudomorphic films grown on Cu(100). Simultaneously, we monitor the distribution of states in momentum space at the Fermi energy. The Fermi surface topology confirms that the films are of fcc symmetry, although tetragonal distortion occurs with increasing Fe moment. The dichotomy in the magnetic behavior is discussed in the light of these, and other recent results. @FootnoteText@ @footnote 1@ C. Roth et al., Phys. Rev. Lett. 70, 3479 (1993). @footnote 2@ R.F. Willis et al., Phys. Rev. B, in press (2000) @footnote 3@ P. James et al., Phys. Rev. B 59, 419 (1999).

9:40am **MI-MoM5 X-Ray and Neutron Scattering Studies of Magnetic Roughness in Thin Magnetic Films*, S.K. Sinha,*** Argonne National Laboratory*; S.A. Stepanov,* Illinois Institute of Technology & Argonne National Laboratory*; R.M. Osgood,* Argonne National Laboratory **INVITED**

It has become apparent that magnetic roughness at interfaces plays an important role in, for instance, the magnetic and transport behavior of thin film magnetic devices. Reflectivity and diffuse scattering studies of thin films using neutrons or X-rays can be used to distinguish between chemical and magnetic roughness at interfaces and to determine the parameters characterizing the latter, such as the correlation length. We discuss the theory of magnetic scattering of neutrons and resonant X-rays by rough interfaces within the Born and Distorted Wave Born Approximations and illustrate how it has been used to analyze experimental results attained on several systems so far.

10:20am **MI-MoM7 Diffuse X-Ray Resonant Magnetic Scattering (DXRMS) of Thin Magnetic Films on Anisotropic Substrates*, J.J. Kelly IV,*** *D.E. Savage, F. Liu, F. Flack, M.G. Lagally,* University of Wisconsin, Madison

Recent applications of very thin magnetic films and magnetic multilayers, such as in magneto-electronics or magnetic data storage, have emphasized the necessity of understanding the nature of magnetism at surfaces and interfaces. For example, the effect of surface and interface morphology, both chemical and magnetic, on spin dependent electron scattering, and thus spintronics devices, is a critical question. Diffuse x-ray resonant magnetic scattering (DXRMS), a unique element-specific technique, provides information on both the chemical and magnetic morphology at surfaces and interfaces by looking at the diffuse and specular components of resonant magnetic x-ray scattering. Using DXRMS and the magneto-optical Kerr effect (MOKE), we have investigated the influence of deliberately induced anisotropic morphology on the magnetic properties of thin magnetic films and multilayers. Changes in x-ray scattering and coercivity are observed as the sample is rotated relative to the incident x-ray beam, and correlated with morphology. The results are discussed in light of previous results using DXRMS and theory. @FootnoteText@ Research supported by NSF and Seagate.

10:40am **MI-MoM8 Control of Surface Roughness during Nanoscale Multilayer Deposition by Adding Surfactants*, X.W. Zhou,*** The University of Virginia*; W. Zou, H.N.G. Wadley,* The University of Virginia, usa

Nanoscale multilayers often exhibit special properties not possessed by their bulk constituents. For instance, multilayers composed of a thin (~20 Å) conductive layer (such as Cu) sandwiched between thin (~50 Å) ferromagnetic layers (e.g., Co) undergo a larger drop in electrical resistance under an external magnetic field. This property, called magnetoresistance, has been utilized in hard drive read heads to allow a significant increase in hard drive storage capacity, and are being explored for nonvolatile random access memories. The performance of these devices can be improved when the interfacial roughness and interlayer mixing of the multilayers can be reduced. While hyperthermal energy deposition techniques have been used to grow the nonequilibrium flat interfaces in the nanoscale multilayers, considerable interests are also growing in searching new multilayer material systems that intrinsically generate low interfacial roughness and interlayer mixing. Traditional material search criteria primarily based upon lattice-match, magnetic saturation, and thermal immiscibility resulted in high quality NiCo/Cu/NiCo multilayers. Better multilayers are likely to be formulated among more complex multilayer structures involving more elements. However, the tremendous possibilities of complex multilayer systems preclude a mere experimental trial and error search for the multilayer systems. Using an atomistic simulation approach, the effects of adding Ag and Au in the NiCo/Cu/NiCo multilayers have been explored. Remarkable Ag surface segregation and surface flattening effects were observed. These surfactant effects were found to be much less for Au. Analyses indicated that such effects can be attributed to the larger size (compared to Cu, Ni, and Co) and lower cohesive energy (compared to Cu, Ni, Co, and Au) of Ag atoms. This finding suggested a new set of materials that should be explored in experiments.

Manufacturing Science and Technology
Room 304 - Session MS-MoM

Metrology for IC Manufacturing

Moderator: G.W. Rubloff, University of Maryland

8:20am **MS-MoM1 Inline Quality Analysis in MBE Manufacturing of AlGaAs/InGaAs pHEMT Structure Using Photoreflectance and Contactless Electromodulation Spectroscopy*, G. Zhou*,** *W. Liu, M. Lin,* Alpha Industries, Inc.

Molecular beam epitaxy (MBE) has become a predominate technology in the manufacturing of pseudomorphic high electron mobility transistors (pHEMTs) for microwave power amplifiers and switchers. In order to keep ahead of the performance and cost curves, nondestructive inline metrologies which leverage the yield learning curve of the fabricator are required. We report the study of implementation of photoreflectance (PR) and contactless electromodulation spectroscopy (CER) as inline quality monitoring tools for AlGaAs/InGaAs pHEMTs manufacturing. Using the reduced mass deduced from experiments, the built-in electric field, the band-gap and/or Al composition in the barrier region is obtained from the above band-gap Franz-Keldysh oscillations (FKO). Two dimensional electron gas (2DEG) density can also be determined by the line shape fitting of the transitions from InGaAs region, and the statistical data both from PR/CER and Hall measurements on a number of wafers are compared. The quality of the device structure and 2DEG density confined within the InGaAs quantum well are found to have a direct relationship both to the intensity of PR/CER transitions from AlGaAs/GaAs superlattice and the built-in electric field in the AlGaAs barrier layer. This observation reveals the possibility to use PR/CER as a screening technique.

8:40am **MS-MoM2 Three Dimensional Reconstruction Metrology by Combinatory Multiple Parameter Characterization and Scanning Probe Microscopy*, E.C. Houge,*** Lucent Technologies and University of Central Florida*; J.M. McIntosh, J.E. Griffith,* Bell Laboratories*; L.A. Giannuzzi,* University of Central Florida*; J.B. Bindell,* Lucent Technologies

Critical dimension metrology of integrated circuits has historically constituted only single parameter characterization of SEM intensity line profiles, which was intended to be representative of the overall linewidth. Due to the surjective nature of the intensity line profile, different morphological patterns can be represented by a single parameter thus causing the inability to delineate deviant morphologies. As the linewidths continue to decrease smaller variations begin to have significant impact in the overall morphology of the linewidth and the pattern transfer function. Three dimensional reconstruction metrology leverages the advantageous of two next generation inline metrology techniques, multiple parameter characterization and scanning probe microscopy, to create a new methodology of metrology. Multiple parameter characterization of scanning electron microscope intensity line profiles initially has shown promise of being able to distinguish deviations from nominal profiles in the characterization and evaluation against preset process margin templates stored in memory. Inline scanning probe microscopy presents the ability to do morphological shape evaluation by nondestructive cross sectioning of critical dimension features obtaining topographic z(x,y) mapping as a function of planar positioning of the scan system. Through the use of these two techniques along with transform reconstruction, a three dimensional topography of the sample surface can be reconstructed utilizing only two dimensional intensity and topographic mapping of the sample surface. Single parameter characterization is then replaced by the determination of Scale (nm), Shape Quality (A weighted polynomial of process margin template deviation, 0-1), and Deviation Bin (A descriptor for type of deviation, A-Z). This segregation of shape and scale along with the full characterization of the feature morphology presents the possibility for the feedback and feedforward use of metrology.

9:00am **MS-MoM3 Application of Scanning Capacitance Microscopy to the Characterization of Semiconductor Device Operation***, **C.Y. Nakakura**, D.L. Hetherington, M.R. Shaneyfelt, P.E. Dodd,* Sandia National Laboratories

Scanning capacitance microscopy (SCM) has become increasingly used for the study of semiconductor doping due to its ability to measure two-dimensional free carrier profiles with nanometer-scale resolution. The bulk of recent SCM work has focussed on carrier profile measurements in cross-sectioned, metal-oxide-semiconductor field-effect transistors (MOSFETs); however, limitations in the hardware and sample structures have restricted most studies to non-functioning devices. To address this, we have modified a commercial SCM and fabricated specially designed test structures that provide independent electrical access to the device regions, enabling the use of SCM to study actively biased devices. By recording images while incrementally increasing the gate bias voltage, we were able to visualize devices switching between the off and on states. The evolution of the SCM images as a function of operating bias provides insight into changes in the channel region during MOS device operation and will be presented in movie form. Complications in image formation, which arise from biasing the device, will be discussed. @FootnoteText@ This work was performed at and supported by Sandia National Laboratories under DOE contract DE-AC04-94AL85000. Sandia National Laboratories is a multi-program laboratory operated by Sandia Corporation for the United States Department of Energy.

9:20am **MS-MoM4 Metrology with Electron Beams - The Current State and Future Directions***, **D.C. Joy**,* University of Tennessee and Oak Ridge National Laboratory **INVITED**

Electron beam tools have become the instruments of choice for CD metrology, as well as for defect detection and analysis, because of the many benefits that they offer. As a result of intensive development work the performance of CD-SEMs and related tools has kept pace with the rapid decrease in feature size and the demands for increased throughput. However with the imminent advent of 100nm design rules in 2003 and the requirement for measurement precisions as low as 1nm and the need to detect defects as small as 10nm, it is clear that this situation is changing because the scope for further enhancements in microscope performance is now small. For example, at low beam energies the SEM is now operating at close to the minimum probe diameter set by diffraction, and the physics of electron-solid interactions and of secondary electron generation set a limit to resolution which may be as poor as 3 to 5nm in materials such as resists. Although some incremental improvements can be anticipated, through new technologies such as aberration corrected lenses, and new ultra-bright electron emitters, these advances will not be sufficient to bring the instruments to the levels required for sub-100nm devices and they will certainly not be sufficient to ensure a continued development path to even smaller structure, and the new molecular devices envisioned beyond the end of the road map. Some radical new solutions must therefore be examined. This talk will therefore examine several possible solutions including the use of high beam energies. the replacement of imaging by holographic techniques, the use of energy filtered imaging methods, and the use of point projection microscopes.

10:00am **MS-MoM6 Limitations of SIMS Depth Profiling for Shallow Implant and Thin Gate Dielectric Metrology***, **M.G. Dowsett**,* University of Warwick, UK **INVITED**

SIMS depth profiling is now expected to extract accurate quantitative data from the top 10 nm of a wafer under circumstances where a significant part of the measurement may be in the top 3 nm, and where the total impurity level in the material may be above 1%. The reality is that, however reproducible the data, accurate profiles can only in general be obtained for impurity levels below 1% and in the depth range 3-10 nm by very careful selection of the analytical conditions. For high dose, ultra-shallow, implants using molecular ions such as BF@sub 2@ (where the total impurity level may be as high as 30%) or for thin (1-5 nm thick) dielectric layers the inherent nonlinearity of both sputtering and ion emission, combined with the fact that the region of interest overlaps with the transient region leads to very strong matrix effects for which no correction procedure has yet been devised (indeed, depending on the level of non-linearity, no correction procedure may be possible). Given that there is an insatiable demand for profiles from the problem region outlined above, how can one obtain accurate profiles, or at least establish the level of error in, say, the dose, junction depth, or internal profile from a 2 nm thick oxynitride layer? The general answer is to examine profiles obtained under different analytical conditions and from different analytical techniques to see if the data converge on a dose or even a shape, to measure changes in erosion rate in the transient region using techniques other than SIMS (e.g. MEIS), and to compare directly profiled data with data where the transient has been removed from the problem by capping the wafer. In addition, measurements should be made under the most linear conditions possible so that reasonable correction procedures can be devised. Of course, suitable reference materials are required, in order to establish such conditions. Techniques for accurate profiling of the top few nm of a wafer still require research and further development of the tools before claims to a reproducible dose and junction depth can be translated into a known accuracy in profile shape, dose and junction depth.

Nanotubes - Science and Applications
Room 309 - Session NM+NS-MoM

Carbon Nanotubes: Functionalization and Applications

Moderator: P.M. Ajayan, Rensselaer Polytechnic Institute

8:20am **NM+NS-MoM1 Surface Interactions Used to Probe Metallic Carbon Nanotubes***, **M. Dresselhaus**,* MIT **INVITED**

A brief overview will be given of the remarkable structure and properties of carbon nanotubes and how surface interactions are used for some of these studies. Carbon nanotubes are tiny structures of molecular dimensions in the form of hollow cylinders with about 20 carbon atoms around the circumference of the cylinders and microns in length. The unique electronic properties of carbon nanotubes are that they can be either semiconducting or metallic depending only on their geometry. From this, stem other remarkable and unique properties of their vibrational spectra, allowing us a means to distinguish metallic from semiconducting nanotubes in samples containing both. Interactions of the nanotubes with nanostructured metallic substrates have provided a powerful tool to gain a fundamental understanding about why the Raman spectra of metallic nanotubes are different from those for semiconducting nanotubes. Though less than a decade since their discovery, carbon nanotubes are already finding practical applications based on their unique properties.

9:00am **NM+NS-MoM3 Purification and Functionalization of Single-wall Carbon Nanotubes***, **I. Chiang**, R. Saini, J. Margrave, R. Hauge, R.E. Smalley, R. Billups,* Rice University

A purification method has been developed which leads to 99.9% pure single wall nanotubes. It combines the well-known nitric acid treatment with water reflux and a two-stage gas-phase oxidation. Air oxidation of SWNTs is correlated to the amount of metals in the samples. For sidewall fluorinated SWNTs, two distinct types of C-F bonds have been observed, ionic and covalent bonds. These 'fluorotubes' have served as precursors for further substitution on the nanotubes, such as sidewall alkylation etc. The degree of substitution is found to correlate with the extent of covalent sidewall C-F bonding.

9:20am **NM+NS-MoM4 Chemical Functionalization of Single-Walled and Multi-Walled Carbon Nanotubes through Ion Bombardment: Predictions from Molecular Dynamics Simulations Nanotubes***, B. Ni, **S.B. Sinott**,* The University of Kentucky

Molecular dynamics simulations have been performed to study the bombardment of single-walled and multi-walled (double and triple) nanotube bundles by CH@sub 3@@sup +@ ions at impacting energies 10, 45, and 80 eV. The reactive empirical bond order potential for hydrocarbons was used in the classical simulations.@footnote 1@ The simulations predict that there is a high probability of radical or fragment adsorption to the nanotube walls which could serve as precursors to the chemical functionalization of the nanotube walls.@footnote 2@ In addition, the simulations show that ion bombardment at 80 eV can lead to cross-linking among the single-walled nanotubes that could stabilize the bundle relative to shear. The multi-walled nanotubes are predicted to be stiffer to scattering than the single-walled nanotubes, leading to increased fragmentation of the incident ions at lower energies. The results are compared to preliminary experimental results for the ion bombardment of muli-walled nanotubes and found to be in good agreement. This work was supported by the NSF (CHE-9708049 and the NSF MRSEC at the University of Kentucky, DMR-9809686) and by the NASA Ames Research Center (NAG 2-1121). @FootnoteText@ @footnote 1@S.B. Sinnott, L. Qi, O.A. Shenderova, D.W. Brenner, in Chapter 1 of Volume IV of ADVANCES IN CLASSICAL TRAJECTORY METHODS, Molecular Dynamics of Clusters, Surfaces,Liquids, and Interfaces, Ed. W. Hase (JAI Press, Inc., Stamford, CT, 1999), pp. 1-26. @footnote 2@B. Ni and S.B. Sinnott, Physical Review B 61, 2000 (in press).

9:40am **NM+NS-MoM5 A Novel Mechanism of Hydrogen Storage in Carbon Nanotubes*, Y.H. Lee,* *S.M. Lee,* Jeonbuk National University, Korea

We have carried out systematic calculations for hydrogen adsorption and storage mechanism in the nanotubes. Hydrogen atoms first adsorb on the tube wall in an arch type and zigzag type up to a coverage of @theta@=1.0, and are stored in the capillary as a form of H@sub 2@ molecule at higher coverages. Hydrogen atoms can be stored dominantly through the tube wall by breaking the C-C midbond, %with relatively low activation barrier of 1.51 eV, while preserving the wall stability of a nanotube after complete hydrogen insertion, rather than by the capillarity effect through the ends of nanotubes. In the hydrogen extraction processes, H@sub 2@ molecule in the capillary of nanotubes first dissociates and adsorbs onto the inner wall, and is further extracted to the outer wall by the flip-out mechanism. Our calculations describe suitably an electrochemical storage process of hydrogen, which is applicable for the secondary hydrogen-battery.

10:00am **NM+NS-MoM6 Local Solvation Shell Measurement in Water using a Carbon Nanotube Probe**, *S.P. Jarvis,* JRCAT-NAIR, Japan*; T. Uchihashi,* JRCAT-ATP, Japan*;* ***H. Tokumoto,*** JRCAT-NAIR, Japan

Oscillatory forces between two approaching surfaces in solvent have long been the subject of study due to their possible influence on any surface-surface interactions mediated through a liquid or in the presence of a fluid film. Of particular interest is water, due to its omnipresence in all but the most stringently controlled environments and its role as the primary medium for biological interactions. Combining a carbon nanotube probe with an AFM has enabled us to measure oscillatory forces in water on approaching a surface that has been laterally characterized on a nanometer scale. One important aspect of the utilization of carbon nanotubes as the AFM probe is to remove the unwanted hydrodynamic damping effect caused by the bulk of the tip. We used a multi-walled carbon nanotube attached to a PtIr coated silicon lever in a specially designed FE-SEM. Another aspect is the usage of a magnetically activated AFM, which has been possible to resolve molecular layers of large molecules. With this method, magnetic material is deposited directly behind an AFM tip on the back-side of the cantilever so that the tip position can be controlled by the addition of a magnetic field. The lever can be vibrated in an oscillating magnetic field in order to make dynamic measurements. This success opens up the possibility of investigating water layers under a variety of experimental conditions and as a function of precise lateral position on any surface including biological membranes and macromolecules. Among the many and varied roles of water layers are effects on biomolecular adhesion, colloid dispersion and tribology, which can now be investigated with nanometer lateral resolution.

10:20am **NM+NS-MoM7 Single Wall Nanotube Probes for Structural and Functional Imaging in Fluid***, **L. Chen**, J. Hafner, C. Cheung, C.M. Lieber,* Harvard University

Scanning force microscopy is a powerful tool for probing nanometer scale objects in fluid, ambient and vacuum environments. The contrast of SFM is based on the interaction between surface and probe which is additive over a wide spectrum of forces including Van der Waals, electrostatic and magnetic forces. Therefore, the resolution of SFM imaging greatly depends on the geometrical and mechanical properties of the probes. Carbon nanotubes make potentially ideal tips for SFM. First, carbon nanotubes can give unprecedented high resolution in structural imaging because of the intrinsic small diameters, high aspect ratio and reversible buckling. Second, carbon nanotubes can be functionalized to give chemically well-defined SFM probes, which enables functional or chemically sensitive imaging. Here we report recent progress in addressing critical issues associated with nanotube probes including the preparation of nanotube tips, structural imaging in fluid, and the functionalization of nanotube ends. Nanotube probes have been prepared by chemical vapor deposition (CVD) on commercial cantilever-probe surfaces. CVD nanotube probes have been used to image individual molecules of supercoiled DNA plasmid pBR322 on mica-fluid interface with high resolution. The relaxation of the supercoiled molecules was observed in real time in aqueous buffer solution. The chemical functionality of the nanotube end group was identified as carboxylic groups, by carrying out force titration experiments. Nanotube probes have been functionalized with synthetic oligonucleotides, and the resulting probes were capable of recognizing complementary oligonucleotide strands on surfaces. The force needed to unbind the 14 base pair duplexes was shown to be 450pN, which is in agreement with previous chemical force microscopy measurements.

10:40am **NM+NS-MoM8 Nonlinear Optical Properties of Some Polymer/Multi-walled Carbon Nanotube Composites***, **Z.X. Jin,*** National University of Singapore, Singapore*; X. Sun, G.Q. Xu, S.H. Goh, W. Ji,* National University of Singapore

Several polymer-coated and polymer-grafted multi-walled carbon nanotubes(MWNTs) were synthesized and characterized using TEM and HRTEM. The polymer-coated or polymer-grafted MWNTs formed stable solutions in DMF. Their nonlinear optical properties were investigated using 532 nm nanosecond laser pulses. These polymer-MWNT composites still possess strong nonlinear optical properties.

Plasma Science and Technology
Room 311 - Session PS-MoM

Plasma-Surface Interactions I

Moderator: E.R. Fisher, Colorado State University

8:20am **PS-MoM1 Plasma-Assisted Etching Processes for Dielectric Materials: Technological Challenges and Elementary Processes on Planar Surfaces and in Microstructures***, **G.S. Oehrlein,*** University of Maryland **INVITED**

Low pressure discharges are used for pattern transfer into dielectric layers in integrated circuit production, e.g. for etching of vias and trenches in the formation of multi-level interconnection schemes. The dielectric materials range from conventional SiO@sub 2@ and different spin-on glass films, organic insulators to porous materials. The control of plasma-surface interactions is a prerequisite for successful pattern transfer into the dielectric materials. We will review the challenges that exist for several prototypical pattern transfer applications, the dominant plasma-surface interaction mechanisms, and the technological solutions that have been demonstrated.

9:00am **PS-MoM3 Observation of Surface Reaction Layers formed in Highly Selective SiO@sub 2@ Etch Process***, **M. Matsui**, T. Tatsumi, M. Sekine,* Association of Super-Advanced Electronics Technologies (ASET), Japan

We characterized the surface reaction layers formed by a fluorocarbon plasma for SiO@sub 2@ selective etching over Si and Si@sub 3@N@sub 4@, in order to understand the etch mechanism and to develop a process and tool for future ULSI processing. Specimens were etched using C@sub 4@F@sub 8@/Ar/O@sub 2@ plasma in a dual-frequency (27/0.8MHz) parallel-plate RIE system. The relationship between ion energy (assumed to be equal to peak to peak voltage (V@sub pp@) of rf bais) and the thickness and composition of the surface reaction layers were quantitatively analyzed using X-ray photoelectron spectroscopy (XPS) and transmission electron microscopy (TEM). The CF polymer layer and the SiF@sub x@O@sub y@ layer on the substrates were observed. We found that the etch rate is strongly affected by the ion energy and the thickness of the CF film on etched materials. In a highly selective etch process, the thickness of the CF layer on the SiO@sub 2@ surface is below 1 nm, while those on the Si@sub 3@N@sub 4@ and Si substrates are about 5-6 nm. The difference in the CF layer thickness on each material should be an origin of the selectivity. Both TEM and XPS observations revealed that reaction layers (2-4 nm) were formed at the interface between the CF layer and Si, Si@sub 3@N@sub 4@. The XPS analysis showed the composition of the reaction layer was SiF@sub x@O@sub y@. This SiF@sub x@O@sub y@ layers were thicker when the ion energy was high and the CF film was thin, i.e. a high etch rate condition for Si and Si@sub 3@N@sub 4@. SiF@sub x@O@sub y@ is thought to be an intermediary product of the Si@sub 3@N@sub 4@ and Si etching. In a highly selective etch process, CF film are so thin that ion energy is not reduced when ions pass through the film on SiO@sub 2@. On the other hand, at the surface of Si@sub 3@N@sub 4@ and Si, thicker CF film were formed and reduced the etch rate, resulted in thin SiF@sub x@O@sub y@ layer formation. @FootnoteText@ This work was supported by NEDO.

9:20am **PS-MoM4 Early-stage Modification of SiO@sub 2@ Surface in Fluorocarbon Plasma for Selective Etching Over Si**, ***K. Ishikawa***, *M. Sekine,* Association of Super-Advanced Electronics Technologies (ASET), Japan

To understand the surface reaction mechanism that governs SiO@sub 2@ etch performance, we studied the surface evolution, starting at the very beginning of the etching process. We also studied the way in which fluorocarbon (CF) polymer reaches a steady-state at a specific thickness. For this purpose, we prepared a modified GEC reference cell and optical apparatus for in-situ time-resolved infrared attenuated total reflection (IR-

ATR) spectroscopy with a germanium (Ge) substrate. The SiO@sub 2@ film was formed by plasma oxidation of Si sputtered on a Ge substrate. We made the SiO@sub 2@ film about 10 nm thick because, according to Fresnel's formula, the CF peak height is linearly proportional to CF film thickness when the underlying SiO@sub 2@ is less than a few hundred nm thick. While the SiO@sub 2@ film was being etched in Ar-diluted C@sub 4@F@sub 8@ plasma, we took spectra every two seconds. A peak, located at 1230 cm@super -1@, due to C-F stretching absorption and a trough, at about 1100 cm@super -1@, due to Si-O stretching absorption, were observed. Observations proved difficult due to an overlap between the two components. By decomposing the spectra, we obtained the separated intensities of the CF and SiO@sub 2@ films. The time-dependence observations were fitted to a model, which enabled us identify the factors that enhance and inhibit CF film growth during SiO@sub 2@ etching. @FootnoteText@ This work was supported by NEDO.

9:40am **PS-MoM5 Silicon Etch Yields and Etching Chemistry in F@sub 2@, Cl@sub 2@, Br@sub 2@, and HBr High Density Plasmas*, S.A. Vitale*[1]**, *H.H. Sawin,* Massachusetts Institute of Technology

Etch yields of silicon in F@sub 2@, Cl@sub 2@, Br@sub 2@, and HBr high density plasmas have been measured as a function of ion bombardment energy, ion bombardment angle, and plasma composition. This information forms a database of experimental values needed for feature profile evolution modeling. For all plasma chemistries, the etch yield increases with the square root of ion energy. Pure Cl@sub 2@ and pure HBr plasmas have very similar etch yields. Silicon etch rates are lower in HBr plasmas than in Cl@sub 2@ plasmas due to lower ion fluxes, not lower etch yields. The dependence of the etch yield on ion bombardment angle is significantly different for Cl@sub 2@ and HBr plasmas. The etch yield in Cl@sub 2@ plasmas decreases rapidly for ion angles above 60° (measured form the surface normal), which results in significant ion scattering from the sidewalls, causing the sidewall bowing and microtrenching seen when patterning polysilicon with Cl@sub 2@ plasmas. The etch yield in HBr plasmas decreases more gradually with ion angle, resulting in less ion reflection from feature sidewalls and could explain the lack of sidewall bowing and microtrenching seen when patterning polysilicon with HBr plasmas. HBr plasmas have higher etch yields than Br@sub 2@ plasmas due to: 1) the higher volatility of SiH@sub x@Br@sub y@ products compared to SiBr@sub 4@, and 2) extra Si surface coverage by small H atoms. As the temperature of the silicon increases, the etch yield in HBr plasmas decreases, due to reduced surface coverage by adsorbed Br and H atoms.

10:00am **PS-MoM6 Studies on SiF@sub x@ Radicals in Fluorosilane Plasmas Used for Silicon Etching and Deposition*, K.L. Williams***, *E.R. Fisher,* Colorado State University

Fluorosilane plasmas have been used in the microelectronics industry for etching of Si/SiO@sub 2@ and for deposition of fluorinated silicon alloys, such as a-Si:H,F. Specifically, fluorinated a-Si films are used in the fabrication of solar cells, photoreceptors, and thin film transistors. In spite of high quality film production, there is still controversy over the mechanistic aspects of deposition processes. Moreover, fundamental chemical and physical information on plasma species such as SiF@sub x@ radicals is not available. The surface reactivity of SiF and SiF@sub 2@ radicals during plasma processing of silicon-containing substrates using the Imaging of Radicals Interacting with Surfaces (IRIS) technique is reported. The molecular beam sources are 100% SiF@sub 4@, 90/10 SiF@sub 4@/H@sub 2@, and 50/50 SiF@sub 4@/H@sub 2@ plasmas. SiF and SiF@sub 2@ have been studied as a function of applied rf power (20, 40, 80, and 170 W) in each of these plasma molecular beams. Initial reactivity measurements of SiF on a Si substrate demonstrate that applied rf power has a significant effect on SiF scatter, which ranges from S = 0.05 at 20 W to S = 0.70 at 170 W. A S < 1 indicates that there is surface loss of SiF. Several possible mechanisms exist which may explain surface loss of SiF . These possible mechanisms will be discussed along with IRIS results for both SiF@sub 2@ and SiF scatter. Furthermore, IRIS results can be correlated with data from film characterization by Fourier transform infrared spectroscopy (FTIR) and profilometry of films deposited under various plasma parameters (applied rf power and % H@sub 2@ addition).

10:20am **PS-MoM7 Ion Energy Distributions at the RF-Biased Electrode in an Inductively-Driven Discharge*, I.C. Abraham***, *J.R. Woodworth, M.E. Riley, P.A. Miller,* Sandia National Laboratories

We report the energy distributions of ions striking an rf-biased electrode in discharges in an inductively-driven Gaseous Electronics Conference Reference cell. The rf-bias and inductive power supplies were phase locked to a 13.56 MHz oscillator. Using a mass-and-energy sensitive ion analyzer we examined the ion energy spectra for ions of a variety of masses in discharges containing mixtures of the noble gases Ar, Ne, and Xe. The ions were sampled thru a pinhole in the rf-biased lower electrode. Oscillations of the plasma potential and the rf-bias waveforms on the driven electrode were directly measured to compare to the ion energy spectra. The ion energy distributions, which had a single peak and a width of 3.5 eV (FWHM) when the electrode was not biased, split into double peaked distributions as rf-bias was applied to the electrode. Lighter ions consistently had larger splittings in their energy distributions, with the largest splittings being in rough agreement with the rf potential difference between the plasma and the biased electrode. The influence of ICP coil power, rf-bias power, and pressure were investigated. Measurements of plasma densities and temperatures as well as comparisons to model ion energy distributions will be presented. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract DE-ACO4-94AL85000.

10:40am **PS-MoM8 The Influence of High Density Plasma on TiN Films Deposited by Ionized Physical Vapor Deposition*, D. Mao***, *J.A. Hopwood, K. Tao,* Northeastern University

The deposition of adhesion layers, diffusion barriers, and seed layers into high-aspect-ratio features is a critical technology for next-generation integrated circuit interconnects.@footnote 1@ One promising method of fabricating high-aspect ratio vias is ionized physical vapor deposition(I-PVD). Titanium nitride films were prepared by I-PVD in a gas mixture of argon and nitrogen. To understand the deposition mechanisms, optical emission spectroscopy analysis, Langmuir probes, and quadrapole mass spectrometry(QMS) were utilized to characterize the plasma. From the results of QMS, the dissociation of N@sub 2@ is as high as 50% for low N@sub 2@ partial pressure(~1.5mtorr), but decreases to 15% at 3.5mtorr. The properties of the TiN@sub x@ films were investigated by Rutherford backscattering, scanning electron microscopy(SEM), stress measurement, and electrical resistivity measurement. The ability of I-PVD to deposit titanium nitride at the bottom of narrow, deep vias and trenches was characterized by cross sectional SEM. The resistivity was found to increase as the N@sub 2@ partial pressure increases. The stress was found to increase from 1 GPa to 7 GPa as the bias voltage changes from -20V to -50V. The effect of nitrogen on the degree of ionization of sputtered titanium will also be discussed. The effect of dissociation of nitrogen and ion density on the characteristics of the TiN@sub x@ film will be presented by comparison with standard sputtering. @FootnoteText@ @footnote 1@ J. Hopwood, 'Ionized physical vapor deposition of integrated circuit interconnects', J. Physics of Plasmas, Vol. 5, pp 1624 (1998)

Semiconductors
Room 306 - Session SC1+EL+SS-MoM
Chemistry of Silicon Oxides and Nitrides

Moderator: E. Cartier, IBM

8:20am **SC1+EL+SS-MoM1 Atomic-Order Thermal Nitridation of Si(100) and Subsequent Epitaxial Growth of Si*, T. Watanabe***, *M. Sakuraba, T. Matsuura, J. Murota,* Tohoku University, Japan

Atomic-order nitridation by NH@sub 3@ on Si(100) and subsequent Si growth by SiH@sub 4@ were investigated using an ultraclean low-pressure CVD system with a Xe flash lamp. Thermal nitridation on Si(100) at 400°C in an NH@sub 3@ environment with and without the flash lamp light irradiation is explained by Langmuir-type physical adsorption of NH@sub 3@ and nitridation by the adsorbed NH@sub 3@. The nitridation can be enhanced by Xe flash lamp light irradiation, and the N atom concentration tends to saturate to about 2.7x10@super 15@ cm@super -2@. In the Si deposition on the ultrathin silicon nitride, it is found that N desorption from the Si nitride films hardly occurs, and Si grew on silicon nitride, whose N atom concentrations are from about 2x10@super 14@ cm@super -2@ to about 2.7x10@super 15@ cm@super -2@, at 385°C in an SiH@sub 4@ environment with and without the flash lamp light irradiation. The incubation period of Si growth is observed and increases with increasing N atom concentration of the silicon nitride film. On the silicon nitride of N

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

atom concentration of about 2x10@super 14@ cm@super -2@, the incubation period is hardly observed and it is found by RHEED measurements that Si epitaxially grew. Layer-by-layer growth control of silicon nitride is proposed by combining atomic-order nitridation on Si and atomic-layer growth of Si on the silicon nitride.

8:40am **SC1+EL+SS-MoM2 The Role of Inter-dimer Interactions in NH@sub 3@ Dissociation on Si(100) - (2 x 1)***, K.T. Queeney,* Smith College*; K. Raghavachari,* ***Y.J. Chabal****,* Bell Laboratories, Lucent Technologies

The chemistry of gas-phase precursors to film growth on the Si(100) surface in ultrahigh vacuum is often well-described by localized interaction of the adsorbate with a single Si-Si dimer.@footnote 1@ However, our combined experimental and theoretical studies of the dissociation of NH@sub 3@ to form NH@sub 2@-Si-Si-H on this surface reveal that this reaction is in fact governed by a complex set of inter-dimer interactions involving both bare and adsorbate-covered Si dimers. External transmission FTIR spectroscopy allows us to probe both the lower-frequency @delta@(NH@sub 3@) modes of metastable, undissociated NH@sub 3@ and the higher-frequency @nu@(SiH) modes resulting from dissociation. By comparing our experimental results with density functional calculations describing two-dimer clusters, we find that the vibrational spectra can only be interpreted when inter-dimer effects are considered. Specifically, while hydrogen bonding between undissociated NH@sub 3@ and dissociated NH@sub 2@ species renders coupling of adjacent nitrogen-containing groups thermodynamically favorable, kinetic control of the dissociation process yields a predominance of the opposite configuration, resulting from the influence of dissociated species on the buckling of neighboring bare dimers during adsorption. We propose that such adsorbate-induced effects on the electronic structure of neighboring dimers may have general implications for controlling the two-dimensional ordering of reactions on the dimerized Si(100) surface. @FootnoteText@ @footnote 1@ See for example: R. Konecny and D. J. Doren, J. Chem. Phys. 1997, 106 (2426); B. B. Stefanov and K. Raghavachari, App. Phys. Lett. 1998, 73 (824).

9:00am **SC1+EL+SS-MoM3 Quantum Chemical Study of Silicon Nitride Deposition Using Ammonia***,* ***Y. Widjaja****, C.B. Musgrave,* Stanford University

Density functional theory is used to examine the reaction mechanisms of nitridation of the Si(100)-2x1 surface by NH@sub 3@. The surface is modeled using the cluster approximation. A detailed reaction mechanism is investigated including ammonia adsorption and decomposition, insertion of N into Si-Si bonds, and H@sub 2@ desorption. We find that nitrogen prefers to be in the subsurface layer, bonded to three Si atoms. The energy barriers leading to the nitridation of the Si(100) surface are also calculated. The activation barrier of the rate limiting step is found to be higher than the activation barrier for NH@sub 3@ desorption. This confirms the experimental observation that a large fraction of the NH@sub 3@ that dissociates on adsorption will recombine and desorb. Furthermore, we have also calculated the vibrational frequencies of various surface nitride structures. The computed frequencies are then compared with the experimental HREELS spectra. The comparison further allows the unambiguous characterization of the surface species. Using the calculated barriers and frequencies we use transition state theory to estimate a rate for nitridation of the (100) silicon surface. We investigate the validity of the cluster approximation and find that bigger cluster models are necessary to describe the nonlocal electronic effects.

9:20am **SC1+EL+SS-MoM4 Thermal Nitridation of Ultrathin Silicon Dioxide Films Using NH@sub 3@ Gas***,* ***O. Jintsugawa****, M. Sakuraba, T. Matsuura, J. Murota,* Tohoku University, Japan

Nitrided ultrathin SiO@sub 2@ film is attractive as the gate insulator of future MOS devices. In this work, thermal nitridation of thin SiO@sub 2@ films and transport of nitrogen species into SiO@sub 2@ films were investigated. A 30Å-thick SiO@sub 2@ film on Si(100) was formed by wet oxidation at 700°C , and was thermally nitrided for 90min at 750-850°C in NH@sub 3@ gas at 100Pa using an ultraclean low-pressure CVD system. The depth profile of N atom was obtained by the repetition of etching by a 1%-diluted HF solution and XPS measurements. By the thermal nitridation, most of the N atoms were present near the SiO@sub 2@ surface and the N atom concentration was remarkably lower (1/2 and 1/10 at 850 and 750°C, respectively) than that of the nitrided Si surface without the SiO@sub 2@ film. By 850°C nitridation, N atom diffused into the SiO@sub 2@ film and Si substrate nitridation were observed. The N atom concentration was estimated to be 4x 10@super 15@cm@super -2@ on the SiO@sub 2@ surface, 1x10@super 21@cm@super -3@ in the SiO@sub 2@ film, and 8x10@super 13@cm@super -2@ at the SiO@sub 2@/Si interface. Binding energy of N 1s at the SiO@sub 2@ surface and in the SiO@sub 2@ film was shifted 2eV-higher than that at the SiO@sub 2@/Si interface. By 750°C nitridation, the N atom concentration on the SiO@sub 2@ surface was 3x10@super 14@ cm@super -2@ and, in the SiO@sub 2@ film and at the SiO@sub 2@/Si interface, the N atom concentration was less than the detection limit (about 3x10@super 20@cm@super -3@ and 4x10@super 12@cm@super -2@, respectively). This result indicates that the existence of surface oxygen more greatly suppresses the reaction of NH@sub 3@ at the lower temperature. Pressure and time dependence of nitridation on the SiO@sub 2@ surface, in the SiO@sub 2@ and at the SiO@sub 2@/Si interface will be also presented.

9:40am **SC1+EL+SS-MoM5 Probing the Chemistry of Dielectric Thin Film Growth on Si Surfaces***, L.D. Flores,* ***J.E. Crowell****,* University of California, San Diego **INVITED**

The surface and gas phase chemistry involved during dielectric thin film growth of doped and undoped silicon dioxide has been studied using the atmospheric pressure reaction between tetraethoxysilane (TEOS) and ozone. The studies involve low temperature deposition of dielectric thin films using a new atmospheric-pressure chemical vapor deposition (APCVD) reactor utilizing a commercial injector / vent assembly. The APCVD reactor is coupled to a N@sub 2@-purged glovebox and a UHV surface analysis facility equipped with XPS, AES, TPD, and IR spectroscopy capabilities. Gas-phase transmission FTIR spectroscopy measurements were performed in-situ during deposition at 400°C by probing the variable gap region between the 400°C heated Si wafer and the injector. The primary products produced upon reaction of TEOS and ozone are acetic acid, formic acid, formaldehyde, carbon monoxide, carbon dioxide, and water. Reaction of TEOS and oxygen in the gas phase is negligible compared to reactions involving ozone at identical temperatures under these conditions. Potential TEOS / O@sub 3@ reaction products and their reaction with boron and phosphorus containing dopant sources has been investigated in order to clarify their role in the oxidation process and to clarify the chemical mechanism. This was accomplished by following the reaction with ozone of some possible and observed ozonation products in a flow reactor / gas cell using transmission FTIR spectroscopy. The products of acetaldehyde ozonation are shown to be different from pathways leading to acetic acid production during TEOS ozonation. Mechanistic pathways unique to Si-O-C containing species will be presented. The products formed upon introduction of boron and/or phosphorus containing precursors to the process flow will also be discussed.

10:20am **SC1+EL+SS-MoM7 Thickness Control of an Ultrathin Oxide Film on Si(100)2x1 Synthesized by Ozone: A Kinetic Study on Initial Oxidation***,* ***K. Nakamura****, A. Kurokawa, H. Itoh, S. Ichimura,* Electrotechnical Laboratory, Japan

One of the alternative oxidants for the fabrication of an ultrathin silicon oxide film is ozone. Using highly concentrated ozone, we have succeeded so far in synthesizing an oxide film of 2nm on Si(100) at lower substrate temperature (for example, at 350°C). This oxide film has high density equivalent to that of a thermally grown oxide, much smaller thickness of structural transition layers, and can be obtained also by modifying and upgrading an already existing native oxide film.@footnote 1,2@ Moreover, the oxide thickness must be precisely and accurately controlled because of its practical use as a gate oxide film in MOSFET. In this paper, therefore, we will study growth kinetics of initial oxidation by ozone on silicon surfaces in detail. To fabricate an ultrathin silicon oxide film by ozone, clean Si(100)2x1 surfaces at between room temperature and 700°C were exposed to highly concentrated (>80%) ozone. Initial oxide growth was mainly monitored by x-ray photoelectron spectroscopy (XPS). The results indicate different kinetics on each oxide layer. Following to an adsorption on the surface investigated also by second harmonic generation (SHG), oxide growth on each of the first three oxide layers proceeded in accordance with Langmuir kinetics, indicating random adsorption on the active sites on each layer. Within this thickness, oxidation rates on the second and third layers possessed positive values of activation energy, while the growth rate on the first layer showed no activation barrier. Above this thickness, an oxide film by ozone grew in proportion to exposure time instead above the critical substrate temperature of 550°C. These suggest that control of film thickness should be optimized in the first three layers and above the fourth, respectively, due to different growth mechanisms. @FootnoteText@ @footnote 1@ K. Nakamura, S. Ichimura, A. Kurokawa, K. Koike, G. Inoue, and T. Fukuda, J. Vac. Sci. Technol. A 17 (1999) 1275. @footnote 2@ A. Kurokawa, K. Nakamura, S. Ichimura, and D. W. Moon, Appl. Phys. Lett. 76 (2000) 493.

10:40am **SC1+EL+SS-MoM8 FTIR at Liquid/Solid Interfaces: In-situ Studies of HF Etching of SiO@sub 2@ on Si(100)***, **K.T. Queeney,*** Smith College Department of Chemistry*; E.E. Chaban, Y.J. Chabal,* Bell Laboratories, Lucent Technologies

While much important semiconductor surface chemistry--cleaning, passivating and etching--takes place at the liquid/solid interface, the inherent difficulty of probing such interfaces has limited mechanistic understanding of these processes. We have developed a novel experimental setup that allows us to probe semiconductor/liquid interfaces with FTIR spectroscopy, circumventing the limitations of conventional multiple internal reflection spectroscopy to access the full frequency range of interest (850-4000 cm@super -1@), in particular the Si-O vibrational modes between 900 and 1250 cm@super -1@. We have used this capability to study in detail the etching in dilute hydrofluoric acid of SiO@sub 2@ on Si(100), lending new and valuable insight into the details not only of the chemical nature of the Si/SiO@sub 2@ interface, but also of structural aspects of the remainder of the film, including the SiO@sub 2@/air (water) interface. By analyzing spectra acquired sequentially during the etching process, we derive a layer-by-layer picture of the oxide spectral response; correlation of those spectra with changes in film structure are made via optical modeling. Varying the dielectric constant of the overlying medium (i.e. air versus water) allows quantification of spectral sensitivity to effects such as surface roughness. In addition, the in-situ nature of these studies allows us to evaluate the kinetics of the etching process and provides strong evidence for a structurally distinct layer near the Si(100) substrate, characterized by a marked change in vibrational signature, that is resistant to etching.

Semiconductors
Room 312 - Session SC2+EL+SS-MoM
Dissimilar Materials

Moderator: H.A. Atwater, California Institute of Technology

8:20am **SC2+EL+SS-MoM1 Integration of Epitaxial Oxide and Nitride Heterostructures with Dissimilar Substrates by Pd-In Wafer Bonding and Laser Lift-off***, **T. Sands,** W.S. Wong, L Tsakalakos, N.W. Cheung,* University of California, Berkeley **INVITED**

The functionality of integrated microsystems can be enhanced through intimate integration of disparate classes of materials. Combining the best materials for their respective functions (e.g., information processing, light emission/detection, and piezoelectric actuation) without sacrificing materials properties is often only possible if the materials are synthesized and processed separately, and subsequently combined. In this talk, a fast, simple and robust "paste-and-cut" method for accomplishing this integration step is described. The process combines low-temperature transient-liquid-phase (TLP) metal bonding with excimer laser lift-off (LLO) to integrate epitaxial group-III nitride (e.g., AlN and InGaN) and perovskite oxide (e.g., PZT and PMN-PT) heterostructures with virtually any substrate, including polymers, stainless steel, and CMOS silicon. Both the TLP and LLO steps are characterized by minimal heating of the receptor substrate, thus maximizing the range of materials classes that may be intimately combined. In our TLP metal bonding process, donor and receptor substrates are coated with Pd/In bilayers and pressure-bonded at 200°C to achieve a high-contact-area PdIn@sub 3@ intermetallic bond with a melting point above 600°C. The L LO process uses a single pulse from a uv laser (e.g., KrF excimer at 248 nm with a pulse length of 38 nsec), irradiating the film/substrate interface through the transparent substrate (sapphire or MgO), to decompose the film at the interface with the substrate. The short pulse duration enables thermal decomposition of the film interface without significant heating of the receptor substrate. Examples of TLP/LLO paste-and-cut integration, including vertical (In,Ga)N light-emitting diodes on Si, and epitaxial ferroelectric (PZT) films on stainless steel, will illustrate the potential of this integration method for the functional enhancement of microsystems. @FootnoteText@ W.S. Wong is now at Xerox PARC, Palo Alto, CA.

9:00am **SC2+EL+SS-MoM3 Growth of SiGe Alloys on Strain-Engineered Si on Insulator (SOI) Substrates***, **P. Rugheimer**, C.H. Lee, D.E. Savage,* University of Wisconsin, Madison*; E. Mateeva,* Colorado School of Mines*; P. Moran, A. Lal, T.F. Kuech, M.G. Lagally,* University of Wisconsin, Madison

Self-organized 3D islands and misfit dislocations form in order to relieve strain during heteroepitaxial growth of SiGe on Si(001). In this work, we use patterned SOI substrates to mediate strain and influence film morphology. Films are grown, using both MBE and CVD, on lithographically defined mesas with lateral dimensions ranging from 2 to 20 microns patterned onto both 10nm Si on SiO2 bonded-wafer substrates and Si(001) control substrates. We have also grown epitaxial films on SOI substrates with MEMs type cantilevers etched on the surface. These cantilevers create regions of either tensile or compressive stress where epitaxial film growth takes place. Film morphology for the samples is followed in-situ during growth with RHEED and ex-situ post growth with X-ray diffraction, Atomic Force Microscopy (AFM) and Cross-sectional Transmission Electron Microscopy (CTEM). We find that growth on patterned mesas as well as cantilevers results in some elastic strain relaxation. Possible mechanisms, such as short-range viscous compliance, anisotropic strain relief, or mediation of dislocations, will be discussed. Supported by NSF-MRSEC and by ONR.

9:20am **SC2+EL+SS-MoM4 Techniques and Interface Effects in Creating Alternative Substrates using GaAs Wafer Bonding***, **A.M. Cain**, P.J. Hesse, D.R. Thomas, K.G. Eyink, D.H. Tomich, M. Ruddell, T.W. Haas, M.L. Seaford,* Air Force Research Laboratory

Compliant substrate technology offers the promise of allowing epitaxial growth of lattice mismatched semiconductors suitable for use in heterogeneous integration. An essential step in realizing a compliant technology is the adequate bonding of the compliant layer to a suitable handle wafer. This work will describe a new wafer bonding facility that allows for precise control of the bonding parameters such as temperature, pressure, atmosphere, and bond processing conditions. The equipment is built around a vacuum furnace fitted with a controllable piston to apply pressure to the bonding wafers. Bonding can be carried out in vacuum or in a variety of inert or reducing atmospheres. The bond furnace is enclosed in a dry box to reduce particle contamination and to reduce atmospheric interactions with bonding surfaces. The equipment is fully computerized to allow for complex bond processing steps. This equipment has been utilized to investigate the effects of various surface chemical treatments of GaAs wafers prior to the bonding process. The technique of arsenic capping of MBE grown buffer layers has been utilized to bond wafers at temperatures as low as 250 °C. Bonding did not occur at 200 °C in agreement with line of sight RGA data that was used to determine the temperatures at which the arsenic was desorbed from the interfaces of the bonding wafers. The conditions used for bonding will be described and characterizations of the interface quality using transmission infrared microscopy and acoustic wave microscopy will be given. Except for occasional particles in the bond interfaces it is possible with this approach to obtain consistently bonded wafers. Comparisons with other surface treatments such as use of epitaxial ready wafers and wafers prepared using conventional etching techniques known to have approximately 2.5nm of oxide present will also be given.

9:40am **SC2+EL+SS-MoM5 Relaxation of SiGe Films on Silicon-on-Insulator Substrates Utilizing Borosilicate Glass***, **E.M. Rehder,** D.E. Savage, P. Moran,* University of Wisconsin, Madison*; T.S. Kuan,* SUNY at Albany*; M.G. Lagally, T.F. Kuech,* University of Wisconsin, Madison

We have grown epitaxial silicon germanium (SiGe) alloy films and studied the relaxation effects of thin silicon-on-insulator (SOI) substrates. Bond and etchback SOI (BESOI) wafers having a top Si layer of 15nm were fabricated. The insulators in these structures were either SiO@sub 2@, using commercial wafers, or chemical vapor deposited borosilicate glass as the insulator. Si@sub 0.82@Ge@sub 0.18@ films were grown on these substrates by ultra high vacuum chemical vapor deposition at temperatures of 550, 630, and 670°C. Films were grown up to 175nm in thickness, which is beyond the equilibrium critical thickness. The low growth temperatures nonetheless result in metastable strained films. Any observed relaxation during growth was then enabled by the SOI. The relaxation following growth was studied by high-resolution double and triple crystal x-ray diffraction and cross sectional transmission electron microscopy. The growth layers on substrates using the SiO@sub 2@ insulator as well as those grown directly on Si substrates are identical and fully strained. However, SOI substrates utilizing a borosilicate glass with 50% B@sub 2@O@sub 3@ content yielded films in which the film strain was reduced by 30%. Post-growth annealing at temperatures from 700 to 1050°C were employed to promote relaxation. When annealed at 950°C the film on the Si substrate remained largely unrelaxed, while the film on the SiO@sub 2@-SOI substrate relaxed to 50%. Lower temperatures resulted in no relaxation, while annealing at 1050°C allows interdiffusion to occur resulting in additional relaxation. Cross-sectional TEM images of these samples reveal a complex dislocation structure in both the film and substrate. The relationship between the oxide viscosities at these temperatures and the image forces affecting dislocation formation and motion will be discussed.

10:00am **SC2+EL+SS-MoM6 Growth of Single Crystalline AlN on Si(111) using Surface Reconstruction Induced Epitaxy***, **M. Jenkins,** A. Faik,* University of North Carolina*; M.R. Sardela Jr,* University of Illinois*; M.-A. Hasan,* University of North Carolina

AlN is a direct wide bandgap (6.2 eV) material suitable for applications in UV emission and detection. In addition, it has a close lattice constant to GaInN, which provides a tunable band gap for emission in the blue to red region. Moreover, integration of group III-nitrides with Si would enable optical interconnects and high power device fabrication on Si. In this work, we have demonstrated growth of hexagonal single crystalline AlN(001) on Si(111) using surface reconstruction induced epitaxy. The Si(111)7x7 surface was first passivated by deposition of ~0.3 monolayer (ML) of Al at 650-700 °C. Each Al atom bonds to 3 Si atoms on the surface, which give rise to the well-known Si(111)@sr@3x@sr@3 surface. The well ordered, Al-passivated Si(111)@sr@3x@sr@3 surface was then used as a template to initiate epitaxial growth of AlN on Si. Without Al passivation, N would react with the clean Si surface forming amorphous Si@sub 3@N@sub 4@, which provides a disordered template and prevents epitaxial growth of AlN. The growth was conducted by using an atomic N flux from a RF atomic source and thermal deposition of Al from an effusion cell. Reflection of high-energy electron diffraction (RHEED), high-resolution X-ray diffraction and transmission electron microscopy results confirmed the formation of single crystalline AlN. The results showed that epitaxial growth of AlN depends strongly on the Al/N flux ratio, growth temperature, and the RF power.

10:20am **SC2+EL+SS-MoM7 Enhanced Thermal Stability of Au Film on GaN by Thin Cr Interfacial Layer***, **J.H. Kim,** H.J. Kang,* Chungbuk National University, Korea*; C.Y. Kim,* LG CIT, Korea*; J.M. Seo,* Chonbuk National University, Korea

In order to enhance the thermal stability of Au film on GaN, 4 ML of thin Cr layer had been deposited prior to Au evaporation. The AFM image shows that, upon postannealing at 650C, Au overlayer with Cr interlayer still keeps its uniformity without forming either pits or islands, while the same amount of Au without Cr interlayer is agglomerated. The corresponding results of scanning Auger microscopy combined with the high resolution x-ray photoelectron spectroscopy indicate that the interfacial Cr partially mixes with GaN and partially mixes with Au overlayer, and reduces the Schottky barrier height of p-type GaN by 0.4 eV. The core level analyses of Cr 2p, Au 4f and Ga 2p indicate a small portion of Ga species also segregates to the top side of this AuCr alloy overlayer. It has been concluded that the role of Cr interlayer for enhancing thermal stability of Au overlayer is in the gradual relaxation of the strain originating from thermal-expansion-coefficient-difference through diffusing into both sides without losing N species.

10:40am **SC2+EL+SS-MoM8 Effects of Hydrogen on the Properties of Cu(TMVS)(hfac) Sourced CVD Copper Films***, **J. Hong**, D. Yang, S. Shetty, T.S. Cale,* Rensselaer Polytechnic Institute

We describe a study of the effects of hydrogen pre- and post-treatment on films grown by Cu(TMVS)(hfac) sourced Cu CVD on TaN substrates using an LPCVD system. Our previous work@footnote 1,2@ showed that the use of water vapor as a co-reactant during Cu CVD can improve the adhesion between the copper film and the substrate. However, the resistivity and surface roughness of the deposited film were degraded when too much water vapor was introduced, probably due to the formation of Cu oxide. The hydrogen pretreatment is an attempt to reduce the native oxide layer on the TaN barrier layer. Films deposited on pretreated substrates have lower resistivity than those on untreated substrates. We have also studied the effects of hydrogen post-treatment on films grown with various amounts of water vapor as a co-reactant. Film properties depend on the duration of the water vapor flow, and the hydrogen post-treatment baking time and temperature. In all cases, resistivity was decreased after treatment compared to untreated films--an effect that we attribute to the reduction of Cu oxides formed in the film. The effect of hydrogen on the surface roughness depends on the amount of water vapor present during deposition and the length of the hydrogen treatment. We conclude that the resistivity of the Cu films is improved and surface roughness is changed with the use of hydrogen as pre- and post-treatment in Cu CVD process protocols. @FootnoteText@ @footnote 1@ D. Yang, J. Hong and T. S. Cale, in Proceedings of the Advanced Metallization Conference in 1999 (AMC 1999), "Effects of Process Variables on Cu(TMVS)(hfac) Sourced copper CVD films". @footnote 2@ D. Yang, J. Hong, and T. S. Cale, in MRS Symposium Proceedings of the MRS Spring 2000 Meeting, "Evolution of Surface Morphology During Cu(TMVS)(hfac) Sourced copper CVD films".

Surface Engineering
Room 201 - Session SE+TF-MoM

Hard and Superhard Coatings

Moderator: A. Inspektor, Kennametal Inc.

8:20am **SE+TF-MoM1 Plasma Deposition of Hard and Thermal Resistant Coatings in the System Si-B-C-N***, **D. Hegemann,** C. Oehr,* Fraunhofer Institute for Interfacial Engineering and Biotechnology, Germany*; R. Riedel,* Technical University Darmstadt, Germany*; H. Brunner,* Fraunhofer Institute for Interfacial Engineering and Biotechnology, Germany

As a result of covalent bonding, the four elements boron, carbon, nitrogen and silicon can form superhard materials. Considering the well-known diamond-like and cubic boron nitride films, which are limited by their temperature resistance and adhesion, respectively, further research in the as before mentioned system is required. Thus, BCN and SiBCN thin films are very promising candidates which are therefore investigated. A capacitive rf discharge in an asymmetrical but confined geometry is chosen for the deposition experiments to sustain well defined plasma conditions. The bias voltage depending on delivered power and pressure is taken as control parameter. Due to the use of single-source precursors - pyridine borane (PB) and triazaborabicyclodecane (TBBD) for BCN, tris(dimethylamino)silylamino-bis(dimethylamino)borane (TDADB) for SiBCN - relative low substrate temperatures (300°C) can be applied yielding amorphous films. Ar or N@sub 2@ in an excess of 50:1 serves as carrier gas. Both with BCN and SiBCN film deposition, several regimes of different chemical composition become apparent increasing the bias voltage. An influence of the used precursor is merely observed at low biases. At moderate bias voltages films comparable to thermal CVD processes are obtained. Further increasing the bias yields hard coatings up to 13.5 GPa and 30.8 GPa measured by microindentation for BCN and SiBCN, respectively. It is found that the hardness scales mainly with the carbon content of both films, analogously. Annealing the films for 5 h in argon or air exhibits a thermal and oxidation resistance of the SiBCN films exceeding 1200°C. On the other hand, BCN films start to decompose at about 1000°C in argon and 800°C in air. Moreover, the SiBCN films show lower internal stresses (1-2 GPa) compared to BCN, which is attributed to a stabilization effect of sp@super 3@ hybridized carbon by silicon incorporation.

8:40am **SE+TF-MoM2 Structure and Mechanical Properties of Ti-Si-C Coatings Fabricated by Sputtering and Pulsed Laser Deposition***, S.H. Koutzaki, **J.E. Krzanowski,*** University of New Hampshire*; J. Nainaparampril,* Systran, Inc.*; A.R. Phani,* University of New Hampshire

Nano-structured coatings consisting of mixtures of carbide compounds can provide a useful route to developing super-hard materials. Heterogeneous nano-structured coatings can be obtained by either deposition of multilayer structures or by depositing film compositions that undergo a natural phase separation due to thermodynamic immiscibility. In the present work, we have taken the latter approach, and deposited films by RF co-sputtering from dual carbide targets, as well as by pulsed-laser deposition (PLD) using ternary carbide targets. We have examined a number of ternary carbide systems, and to date the most promising coatings have been obtained in the Ti-Si-C system. In this system, the TiC and SiC phases are highly immiscible and phase separation on deposition is likely to occur. We first examined sputter-deposited TiC coatings with varying SiC content. It was found that the nano-indentation hardness increased with SiC content, with a maximum hardness nearly twice that of the sputtered-deposited TiC films at a SiC content of 15 at. %. We further analyzed these films using high-resolution TEM, XPS and X-ray diffraction. Since cubic SiC has an X-ray pattern almost identical to that of TiC, the extent of phase separation could not be determined by that method. However, XRD did demonstrate a general disordering of the films with increasing SiC content. High-resolution TEM also revealed that films of higher SiC content exhibited a mottled structure and nano-scale phase separation within the grains. Further studies were conducted comparing PLD TiC and TiC-12 at.% SiC films (the latter made using a ternary target). The Ti-Si-C coatings exhibited about 25% higher hardness levels in comparison to TiC alone.

9:00am **SE+TF-MoM3 Hard and Superhard Coatings - A Review***, **W.D. Sproul**[1],* Reactive Sputtering, Inc. **INVITED**

Hard coatings such as titanium carbide deposited by the high temperature chemical vapor deposition (CVD) process first made their commercial appearance in the late 1960s. The single layer coatings were soon

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[1] **Featured Speaker - Science and Technology in the 21st Century**

supplanted with multilayer CVD coatings, but it was difficult to apply these coatings to high speed steel (HSS) tooling or steel alloys without damaging the metallurgical properties of the steel. In the early 1980s, several physical vapor deposition (PVD) techniques became available for depositing hard coatings such as titanium nitride or titanium aluminum nitride onto HSS. One of the driving forces in the PVD coatings business has been a desire to increase the hardness of the coatings with the ultimate goal of matching or exceeding the hardness of diamond. Today superhard (hardness greater than 40 GPa) coatings exist. The hardening mechanisms for achieving superhardness fall into two categories, intrinsic and extrinsic. Intrinsic materials such as diamond, cubic boron nitride, and some ternary compounds rely on high bond energies and short bond lengths to achieve superhardness whereas the extrinsic nanostructured multi-layer and nanocrystalline materials rely on the microstructure to restrict dislocation movement to achieve superhardness. A hardness exceeding that of diamond has been reported for a nanocomposite of titanium nitride and silicon nitride. Coating hardness is only one property that should be considered when engineering a surface. Coating toughness should also be factored in especially in situations where impact loading will occur. Today advances are being made in high-density plasma (HDP) PVD techniques that will have a direct impact on future PVD hard coatings. The high degree of ionization in HDP systems will allow new compounds synthesis at temperatures well below the thermodynamic equilibrium point. Perhaps in the near future crystalline alpha alumina will be deposited below 500 degrees C by HDP PVD techniques.

9:40am **SE+TF-MoM5 Unbalanced Magnetron Sputter Deposition of Al-Ti Ceramic Coating for High Speed Milling Application***, **X. Zeng,*** Gintic Institute of Manufacturing Technology, Singapore

Hard coatings for high speed machining consist of multiple layers because of the requirements for high adhesion strength to the substrate, high thermal stability, high hardness and low friction coefficient and good compatibility. Traditionally used coatings like TiN, CrN and their alloyed nitride coatings have high hardness and good adhesion on common tooling materials used in industry. However, these coatings usually have poor performance in high speed machining applications, especially in the cutting of hardened tool steels, because of phase transition (oxidation) at high temperatures. Ti-Al alloyed nitrides seem to be one of the most promising coatings for this application due to its high thermal stability, low friction coefficient and high hardness. This paper reports the development of a multilayered Ti-Al ceramic hard coating on tunsten carbide ballnose endmills for high speed milling using an unbalanced magnetron sputtering system @footnote 1@. The process parameter dependence of the coating properties was studied. X-ray diffractometry, x-ray photoelectron spectroscopy, nanoindentation and scratch test were used to characterize the structural, compositional and mechanical properties of the coatings. High hardness, up to 40 GPa, good adhesion strength, up to 100 N in scratch critical load, and high oxidation resistance were achieved, leading to excellent performance in high speed milling on hardened tool steel at a machining speed of 260 m.min@super -1@. The results show that the tool life with this coating is improved by a factor of 4 or better, under the testing conditions used, compared to the uncoated WC tools. The surface finish of the machined steel achieved with this coating is also significantly better. @FootnoteText@ @footnote 1@ X.T. Zeng, J. Vac. Sci. Technol., A 17, (1999) 1991

10:00am **SE+TF-MoM6 Thermal Stability and Mechanical Properties of Nano-scale W/ZrN Multilayers***, **A. Madan,*** Northwestern University*; J. Ji, S.A. Barnett,* Applied Thin Films, Inc.

Nanolayered thin films show an enhanced hardness and improved mechanical properties as compared to the individual layer components. The high-temperature stability of these films is important for various technological applications e.g. dry-cutting. We report on the thermal stability and mechanical properties of polycrystalline, immiscible W/ZrN nanolayered films. W/ZrN multilayers of bilayer periods 2 to 40 nm were sputter deposited in a dual-opposed-cathode unbalanced-magnetron sputtering system. The W fraction was varied from 0.3 to 0.8 by adjusting the relative power on the two targets. The 1 micron films were annealed at temperatures from 750°C to 1000°C in inert atmospheres. The as-deposited and the annealed films were characterized using x-ray diffraction, cross-sectional transmission electron microscopy (XTEM), and nanoindentation. The as-deposited films showed an enhanced hardness in comparison to the rule-of-mixtures values irrespective of the bilayer period or the layer composition ratio. High- and low-angle x-ray diffraction (XRD) showed that the layered structure was stable after annealing at 1000°C for 1 h. XTEM results for as-deposited and annealed films will be presented. The annealed films show hardnesses as high as 44 GPa. The excellent high-temperature stability of the W/ZrN nanolayered structures arises because W and ZrN are mutually immiscible.

10:20am **SE+TF-MoM7 Growth and Characterization of ZrN/ZrB@sub 2@ Nanolayered Coatings for High Temperature Applications***, **K Martin**, J. Ji, I. Kim, S.A. Barnett,* Applied Thin Films, Inc.*; A. Madan,* Northwestern University*; P. Hedge, A. Inspektor,* Kennametal, Inc.

There is a great need for cutting tool coatings that perform well at elevated temperatures, both because of the desire to cut at higher rates and to eliminate coolant fluids. However, current cutting-tool coating materials fail rapidly under these conditions because of poor high-temperature properties. The ZrN/ZrB@sub 2@ nanolayered system is expected to provide a unique combination of properties including high hardness, excellent stability at elevated temperatures, low chemical solubility in Fe and good thermal expansion match with cemented carbide tools. In this investigation, ZrN/ZrB@sub 2@ nano-layered coatings were deposited using a dual-cathode magnetron sputtering system. The key properties including hardness, adhesion, and residual stress were evaluated as a function of composition, bilayer period, and substrate bias. The hardness values for as-deposited coatings ranged from 30-38 GPa and increased to 49 GPa after annealing at 1000°C. Low and high angle XRD revealed that the superlattice structure was stable at elevated temperatures. The increase in hardness after annealing is attributed to the transition of the soft amorphous ZrB@sub 2@ to the crystalline form. Adhesion testing verified that the coatings adhered well on cemented carbide inserts even after annealing at 1000°C.

10:40am **SE+TF-MoM8 Fabrication of Al-Pt Coating on Ni Base Superalloys and Studies of Their Structure***, M. Ghoranneviss, **H. Parchamy Aragy**,* Islamic Azad University, Iran*; A. Sedghi,* International Iran Khomani University, Iran*; A. Shokohi,* Islamic Azad University, Iran

Thin film coating are formed on the engineering materials to improve their physical and mechanical properties these coating are used mainly in different fields of industrial application and in these respect many research projects conducted to improved their properties.In this research,therefore,the formation of Al-Pt(Aluminum/Platinum)alloys coatings on nickel based super alloys has been studied.Sputtering-ion beam technique under Argon plasma and subsequent heat treatment is been used to fabricate these coating.Ion implantation is applied the Aluminum-Platinum alloys coatings.The main goal of this work is increasing erosion and consequently erosion-corrosion resistance of these coating.Scan Electron Microscope,Glow discharge Spectrometers and X-Ray Diffraction techniques is used to investigate the structure of fabricated coatings.These results correlates with other investigations and these method can be presented as a industrial method for fabrication of these coating.Ion implantation improved these properties but the results not very appreciable.Details will discus in full paper.

Surface Science
Room 208 - Session SS1-MoM

Atomic-Scale Studies of Model Catalysts

Moderator: S.H. Overbury, Oak Ridge National Laboratory

8:20am **SS1-MoM1 STM Study of H - Al (111): From Alane-Formation Reactions to Absorption-Induced Roughening***, **M. Noh,** J.E. Reutt-Robey,* University of Maryland

We investigated the reaction of atomic hydrogen with Al (111) with STM under UHV conditions. We show that hydrogen reacts strongly with the substrate to form aluminum hydride oligomers (alanes) which are stable up to ~350K. At lower reaction temperatures (T< ~230K), the distribution of surface alanes is highly nonuniform, with one dimensional strings of alanes extending for thousands of Å. These strings act as mass barriers that direct the distribution of later-form alanes. The alane strings run roughly parallel to crystallographic steps and exhibit a terrace-width-dependent nucleation. We discuss the physical origin of these intriguing reaction patterns. These surface reactions are accompanied by hydrogen absorption. Subsurface hydrogen is sensed indirectly by regions of increased surface roughness that can eventually leads to delamination. * Supported under NSF contract DMR-9632521 and CHE-9800470.

8:40am **SS1-MoM2 Dynamic Imaging and Chemical Probing on the Atomic Scale: NO/H@sub 2@ and NO@sub 2@/H@sub 2@ on Pt***, T. Visart de Bocarm@aa e@, T. Baer, C. Voss,* ***N. Kruse,*** Universit@aa e@ Libre de Bruxelles, Belgium

The reaction of NO and NO@sub 2@ with hydrogen has been studied on a Pt single crystal using field ion microscopy (FIM) and atom-probe field ion mass spectrometry (APFIMS) under conditions of applied temperatures (395-530 K), pressures (10@super -4@ - 10@super -2@ Pa) and field strength (8.7 V/nm). The 3D-Pt sample ("field emitter tip") has been found to undergo a transformation from a nearly hemispherical shape into a top- and edge-truncated pyramid. Kinetic instabilities, including rapid ignition and oscillations, were found for both reactions on this reshaped crystal. Video-FIM (time resolution: 20ms) revealed the rough areas lying between the (001) top plane and the (111) slopes of the pyramid to be catalytically most active. Catalytic ignition to water production was seen to occur in (012) areas with subsequent wave propagation either predominantly along the (for NO/H@sub 2@) or along the zone lines (for NO@sub 2@/H@sub 2@). Thus in either case a strongly anisotropic reaction behavior was observed. Under oscillatory conditions the catalytic cycles lasted for several 100ms only. The local chemical analysis of (012) and (133) planes (comprising several ten Pt atoms) demonstrated the formation of water product (desorption as H@sub 2@O@super +@ and H@sub 3@O@super +@) during the catalytic cycles. Major amounts of NO@sub x@@super +@ were registered due to surface diffusion of either NO or NO@sub 2@ into sites emptied by either reaction. Moreover, the mass spectrometric results strongly suggest NO@sub x@@super +@ to be the imaging species at otherwise rather low field strengths.

9:00am **SS1-MoM3 STM Studies on Model Systems Relevant for Catalysis***,* ***F. Besenbacher,*** University of Aarhus, Denmark **INVITED**

Scanning tunneling microscopy (STM) has proven to be a fascinating and powerful technique in the field of surface science. The fact that sets STM apart from most other surface sensitive techniques is its ability to resolve single atoms and molecules on surfaces and furthermore to reveal the dynamics of surface processes by recording many sequential STM images with a fast-scanning, variable-temperature STM.@footnote1@ In this talk I will show how STM can be used in the design of new catalysts. More specifically, I will show how STM studies have lead to the design of new alloy catalysts for the steam reforming reaction,@footnote 2@ to atomic-scale information on the sintering of Pt nanoclusters promoted by hydrogen,@footnote 3@ and to a new insight into the morphology and edge structures of MoS@sub 2@ nanoclusters, which are of interest as model systems for hydrodesulfurization catalysts.@footnote 4@ @FootnoteText@ @footnote 1@ F. Besenbacher, Scanning Tunneling Microscopy studies of metal surfaces, Reports on Progress in Physics 59 (1996)1737 @footnote 2@ F. Besenbacher, I. Chorkendorff, B.S. Clausen, B. Hammer, A. Molenbroek, J.K. Norskov and I. Stensgaard, Design of a surface alloy catalyst for steam reforming, Science 279 (1998) 1913 @footnote 3@ S. Horch, H.T. Lorensen, S. Helveg, E. Lagsgaard, I. Stensgaard, K.W. Jacobsen, J.K. Norskov and F. Besenbacher, Enhancement of surface self-diffusion of platinum atoms by adsorbed hydrogen, Nature (1999) 134 @footnote 4@ S. Helveg J.V. Lauritsen, E. Lagsgaard, I Stensgaard, J.K. Norskov, B.S. Clausen, H. Topsoe and F. Besenbacher, The atomic-scale structure of single-layer MoS@sub 2@ nanoclusters, Phys.Rev. Lett. 84 (2000) 95.

9:40am **SS1-MoM5 Reactivity of Carbonate and Chemisorption of Carbon Dioxide on Ag(110):A Combined STM, LEED, and TPRS Study***, X.-C. Guo,* ***R.J. Madix,*** Stanford University

Twenty years have passed since we first indentified the surface carbonate species formed by the reaction of carbon dioxide with preadsorbed oxygen on Ag(110) by isotope-labeled TPRS (temperature programmed reaction spectroscopy) studies. In the intervening years the same system has been extensively investigated by many groups with various surface techniques including LEED, HREELS, XPS, UPS, NEXAFS, and STM. The carbonate species was confirmed and a bonding configuration proposed. However the stoichiometry of this basic reaction has recently come into question as a result of STM studies by three independent research groups - each believing to image the carbonate structure on Ag(110). Here we present new results of a combined STM, LEED, and TPRS study in this laboratory. Carbonate is shown to form at modest exposures of preadsorbed oxygen to carbon dioxide, and its structure is readily imaged. However, a high reactivity of the carbonate toward CO is observed, which leads to a stable chemisorbed state of CO2 chemisorption on a Ag(110)-(1x2) reconstructed surface, in dramatic contrast to the weakly adsorbed physisorbed state of CO2 on Ag(110)-(1x1). Thus high exposures of preadsorbed oxygen to carbon dioxide in ultrahigh vacuum are expected to lead to the formation of this species, since one expects there to be a background CO partial pressure accompanying the carbon dioxide dose. Indeed we have duplicated this result with high CO2 exposures. The STM images of the chemisorbed CO2 we obtain agree precisely with those previously attributed to carbonate by other groups, and they are distinctly different from those of carbonate. The carbonate species was correctly imaged with STM and its formation was followed in situ at 300 K. We also report here on the structure and surface mobility of the chemisorbed CO2 species.

10:00am **SS1-MoM6 Surface Structure and Chemical Properties of a MnO/Rh(100) Model Catalyst***,* ***J. Nakamura,*** *H. Nishimura, J. Ogawa,* University of Tsukuba, Japan*; T. Fujitani,* National Institute for Resources and Environment, Japan

The atomic structure of a MnO-deposited Rh(100) surface was studied using STM and LEED. The STM image of MnO/Rh(100) at a Mn coverage of 0.80 showed two hexagonal MnO domains rotated by 90 degree with respect to each other. One of the unit vectors for these hexagonal domains had same direction as the unit vector of the Rh(100) substrate. An averaged spacing of 0.31 nm was obtained by the STM for the nearest neighbor atoms of the hexagonal layer. The LEED pattern showed two hexagonal domains, which were consistent with the atomic structure observed by STM. The structure of hexagonal monolayer was very similar to MnO(111) in terms of lattice constant and symmetry. Adsorption of CO on the MnO/Rh(100) was studied using in-situ IRAS. Linear and bridge CO was observed on the clean Rh(100) and MnO/Rh(100) surfaces. New peaks or peak shifts were not observed on the MnO/Rh(100) in disagreement with the powder catalyst results of a Mn-promoted Rh catalyst. No IRAS peaks of CO were observed on the MnO/Rh(100) above the MnO coverage of unity, indicating that a monolayer MnO species grew on the Rh(100). The ratio of linear and bridged CO species varied with MnO coverage, suggesting that the surface area of bare Rh(100) planes on the MnO/Rh(100) controlled the ratio. The oxygen of MnO/Rh(100) is readily reacted with CO to form CO@sub 2@ at 300-400 K in UHV. The reaction probability at 373 K is close to unity.

10:20am **SS1-MoM7 Adsorption and Reaction on Oxide-supported Pd, Rh and Ir Particles***,* ***M. Baeumer,*** *M. Frank, S. Shaikhutdinov, H.-J. Freund,* Fritz-Haber-Institut, Germany

Supported metal clusters and nanoparticles are of fundamental and technical interest. One important area of application is heterogeneous catalysis, for example. On a microscopic level, however, there is only limited knowledge about the dependence of adsorption behaviour and catalytic activity on particle size and morphology. In order to contribute to an understanding of these relationships, we have studied oxide-supported Pd, Rh and Ir particles and their interaction with adsorbates. As a support, a thin alumina film grown on NiAl(110) was employed so that scanning tunneling microscopy and electron spectroscopies could be applied without charging problems. The STM results show that particle sizes ranging from a few atoms up to several thousand atoms are accessible via growth under vacuum conditions. By changing the temperature during deposition, disordered as well as crystalline aggregates are obtainable. After having dealt with the structure, we discuss the adsorption and reaction of ethene on these systems. The studies, which have been carried out using infrared and photoelectron spectroscopy, shed light on the formation of differently co-ordinated species and their thermal dehydrogenation. Gradual changes depending on the metal and the particle size are observed. Finally, we turn to the hydrogenation of ethene with hydrogen which has been investigated by thermal desorption spectroscopy.

10:40am **SS1-MoM8 Reactive Intermediate Species on WO@sub 3@ Resolved at the Atomic Scale during Alcohol Dehydration***,* ***R.E. Tanner,*** *P. Meethunkij, E.I. Altman,* Yale University

In order to better relate structure and reactivity on monoclinic @gamma@-WO@sub 3@(001), we have studied reactions on the surface using scanning tunneling microscopy (STM), temperature-programmed desorption (TPD), Auger electron spectroscopy and low-energy electron diffraction. The ordered c(2 x 2) reconstruction may be reproducibly generated by heating in O@sub 2@. The termination of the bulk structure is seen in LEED and STM to correspond to a WO@sub 2@ plane in which half the W@super 6+@ cations are covered by terminal O. The catalytic activity was probed by exposure of the c(2 x 2) surface to a series of alcohols. Methanol, 1-propanol, 2-propanol, and 2-methyl-propan-2-ol (t-butanol) all adsorbed on the surface. The sticking coefficient is similar for all alcohols indicating the ease of deprotonation and formation of alkoxide. TPD showed desorption of water and unreacted alcohol at temperatures less than 600 K, independent of the alcohol. The alkoxide all desorbed as alkenes at higher temperatures, so the c(2 x 2) surface displays only dehydration activity. The peak of the alkene desorption trace decreases from primary to tertiary alcohol (1-propanol --> t-butanol), indicating that desorption is limited by the rate of C-O bond scission of the adsorbed alkoxide, and is independent of the deprotonation rate. STM images revealed terraces covered with adsorbates that have no preference for attachment at steps or other defect sites. Further images are presented where the WO@sub 3@(001)-c(2 x 2) substrate atomic periodicity is seen simultaneously with the alkoxide intermediates. The sites for oxidative dehydration of the alcohol molecules are identified as the exposed five-fold coordinated W@super 6+@ ions on clean terraces, in agreement with the theory of enhanced activity at coordinatively unsaturated sites. The STM tip can be used to remove the alkoxide adsorbates from the surface to reveal the structure of the underlying, reactive adsorption sites.

Surface Science
Room 209 - Session SS2+NS+TF-MoM
Nucleation and Growth

Moderator: G.L. Kellogg, Sandia National Laboratories

8:40am **SS2+NS+TF-MoM2 Homoepitaxial Growth of Ni on Ni(110) : Surface with Anisotropic Diffusivity and Energy Barriers***, **B.-Y. Choi**,* Seoul National University, Korea*; S.-J. Kahng,* University of Illinois at Urbana-Champaign*; J.-Y. Park, Y. Kuk,* Seoul National University, Korea

The homoepitaxial growth of Ni was studied on Ni(110) surface with scanning tunneling microscopy. The Ni(110) surface does not reveal surface reconstruction, but it has corrugated channels along the [1 -1 0] direction and the resultant surface diffusion anisotropy. Homoepitaxial islands grow with high aspect ratio, as large as 1:1000, due to i) the diffusion anisotropy and ii) the energy barrier from an [1 -1 0] side wall to an [001] side wall around the adatom islands. The aspect ratio of the islands decreases with increasing temperature. The competition between these two mechanism will be discussed. At the high coverage (@>=@10ML), the aspect ratio decreases substantially and the growth structure transforms to 3D islands without asymmetry. At these coverage, the surface roughness saturates. Although the microscopic origin is unclear, the phenomenon can be explained with a KPZ type equation with some modifications.

9:00am **SS2+NS+TF-MoM3 Thermodynamics of Thin Film Alloys: Experimental and Theoretical Study of Ag and Co on Ru(0001)***, **G.E. Thayer**,* University of California, Davis*; A.K. Schmid, V. Ozolins, N.C. Bartelt,* Sandia National Laboratories*; S. Chiang,* University of California, Davis*; R.Q. Hwang,* Sandia National Laboratories

It has long been known that the structure of materials in thin film configurations can differ significantly from their bulk phase. This is particularly true of alloy films. It has recently been shown that strain induced by the lattice mismatch between substrate and film can lead to the formation of novel alloys that do not exist in the bulk. One prototypical example is the system of one monolayer Ag/Co films grown on Ru(0001). In the bulk, Ag and Co are immiscible. However, on the Ru surface alloy phases of distinct stoichiometries are formed. We have investigated the phase diagram of 1ML AgCo/Ru(0001) films using scanning tunneling microscopy (STM) and first principles calculations. For Ag rich films, segregation between a pure Ag phase containing dislocations and a pseudomorphically strained alloy of stoichiometry Co@sub 0.6@Ag@sub 0.4@ is found. The driving force for the phase segregation is the competition between two strain relief mechanisms: dislocation formation and alloying. In the Ag saturated Co@sub 0.6@Ag@sub 0.4@ alloy, atomic resolution STM images show that the alloy consists of a Co film containing disordered, elongated Ag droplets with an average size of 30 atoms separated by an average distance of 10 Co atoms. As the composition of Ag in the film is decreased, the Ag droplets become more uniform in size and decrease to an average minimum size of 10 atoms. Simultaneously, the distribution of the droplets becomes uniform and dilute. This behavior has been predicted using first principles, local density approximation (LDA) calculations. These calculations, together with atomically resolved STM images, have quantified configuration energies for various stoichiometries of this system. This investigation has led to a quantitative interpretation of the competition between the chemically repulsive interaction of Ag and Co (also seen in their bulk miscibility gap) and the strain fields in the thin film alloy that they form.

9:20am **SS2+NS+TF-MoM4 Theory of the Nucleation and Growth of Iron on GaAs***, **S.C. Erwin**,* Naval Research Laboratory*; M. Scheffler,* Fritz Haber Institute, Germany

By growing ultrathin films of ferromagnetic metals on semiconductor substrates, it is possible to create a partially spin-polarized electrical current in the semiconductor. This phenomenon is the starting point for a wide variety of magnetoelectronic devices based on the "spin-valve" effect, whereby an externally applied magnetic field can switch the current on and off. Considerable experimental effort has focused on ultrathin films of Fe grown by MBE on GaAs, in part because their small lattice mismatch results in nearly epitaxial films. Although a number of experiments have contributed to a detailed description of the phenomenology of magnetism in these films, little is known about the microscopic physics of magnetism at an intimate metal-semiconductor interface. We use spin-polarized density-functional total-energy methods to investigate the nucleation and initial growth phases of Fe on GaAs(001), focusing on the roles played by diffusion, magnetism, and defect chemistry. Our findings include the following results: (1) magnetism develops in the very first monolayer, and is in fact enhanced by the presence of the interface; (2) surface diffusion is strongly suppressed in the submonolayer regime by the tendency of Fe adatoms to form very stable Fe-As bonds. Finally, we discuss the influence of the initial GaAs reconstruction on the structure and magnetic properties of the Fe film.

9:40am **SS2+NS+TF-MoM5 Nucleation and Growth in Metal-on-Metal Epitaxy - Complications beyond Simple Systems***, **R.J. Behm**,* University of Ulm, Germany **INVITED**

The quantitative atomic scale understanding of a surface process, as a sequence of elementary steps, is one of the primary objectives in Surface Science. Molecular beam epitaxial growth (MBE) is one the first areas where extensive and systematic studies, both experimental and theoretical, have led to such kind of understanding, at least for simple processes such as nucleation and two-dimensional growth on inert, bare and non-reconstructed substrates.@footnote 1@ In this talk I will focus on complications which arise when these conditions are not fulfilled, predominantly on the effect of coadsorbed species on nucleation and growth processes. These coadsorbates, which are generally present, e.g., in the case of chemical vapor deposition (CVD), are shown to affect not only the nucleation behavior, but may lead also to the formation of new, (metastable) film structures. A second topic to be discussed involves nucleation and growth on 'instable' surfaces, where growth competes with exchange processes and surface alloy formation. On such systems and under certain conditions metal deposition was found to cause a severe restructuring of the substrate, leading to pit formation. Mechanistic ideas will be presented and discussed. @FootnoteText@@footnote 1@H. Brune, Surf. Sci. Rept. 31, 121 (1998).

10:20am **SS2+NS+TF-MoM7 Preferential Nucleation of Metal Nanoclusters on S(4x4)/W(111)***, **Q. Wu**, W. Chen, T.E. Madey,* Rutgers, The State University of New Jersey

Interactions of several metals (Cu, Pt and Pd) with the highly ordered S(4x4)/W(111) surface have been studied by means of Auger electron spectroscopy (AES), low energy electron diffraction (LEED), and scanning tunneling microscopy (STM). The substrate is a sulfur-induced nanoscale reconstruction of W(111) with (4x4) periodicity, characterized by broad, planar terraces (~ 30 nm in width). We find that fractional monolayers of vapor-deposited Cu grow as 3D clusters on the S(4x4) surface over a wide coverage range. At low Cu coverages (@<=@ 0.1 ML), Cu nanoclusters are observed to nucleate preferentially at characteristic 3-fold hollow sites on the S(4x4) surface; there is a clear energetic preference for one type of site over others. The formed Cu nanoclusters are uniform in size (~ 0.7 nm) up to 0.25 ML, indicating self-limiting growth. As coverage increases, additional sites are populated and Cu clusters grow in size. On the other hand, Pt and Pd exhibit a different behavior, disordering the (4x4) reconstruction and adsorbing beneath the outer S-layer. STM data are supported by LEED and AES measurements. The data are interpreted in terms of relative surface free energy, relative reactivity, and the metal-W, metal-S, and S-W binding energies, as supported by our previous TPD data.

10:40am **SS2+NS+TF-MoM8 Ultra-thin Al Films Grown Epitaxially on CaF@sub 2@/Si(111)***, **Y.V. Shusterman**, N.L. Yakovlev, L.J. Schowalter,* Rensselaer Polytechnic Institute

Electron scattering at metal boundaries becomes increasingly important as interconnect structures shrink further. To improve our understanding of this phenomenon, studies of electron transport through ultra-thin metal films are needed. In such experiments, it is desirable to have smooth, single crystal metal layers grown on an insulating substrate. For this reason, we are studying epitaxial growth of Al on CaF@sub 2@/Si(111), with metal thickness as low as several nanometers. The structures discussed in this work were grown by molecular beam epitaxy and investigated by reflection high-energy electron diffraction (RHEED), scanning tunneling microscopy (STM) and atomic force microscopy (AFM). Hydrogen-terminated Si(111) was used as a substrate. The CaF@sub 2@/Si interface was formed at 700°C, followed by fluoride overgrowth at temperatures below 200°C, which resulted in improved continuity of the subsequent Al layer. The roughness of the final CaF@sub 2@ surface was below 1nm, as measured by AFM. The Al films grew epitaxially, as revealed by RHEED patterns that only contained streaks. The spacing between the streaks from Al was about 4/3 times larger than that from CaF@sub 2@, in agreement with bulk lattice mismatch. The growth proceeded through formation of 3-dimentional islands that then coalesced as the thickness increased. Using an Al deposition rate above 1nm/s at room temperature, we were able to obtain continuous films as thin as 10nm with roughness less then 2nm. The STM images of these films showed atomic steps, some of them originating at screw dislocations. The density of these dislocations was around 10@super 11@ cm@super -2@. The dependence of Al conductivity on film thickness will also be presented.

Surface Science
Room 210 - Session SS3-MoM

Surface Science Opportunities and New Applications

Moderator: B.E. Koel, University of Southern California

8:20am **SS3-MoM1 Out of the Vacuum - Into the Liquid***, **M. Grunze**[1],* University of Heidelberg, Germany **INVITED**

Motivated by the need to establish a knowledge base for microelectronics and heterogeneous catalysis, Surface Science matured as an interdisciplinary research area at the intersection of solid state physics and chemistry. The available experimental probes and theoretical concepts allow today to study surfaces and interfaces in unpreceded detail under vacuum or controlled gas atmospheres, but are less suitable to investigate surfaces in liquid environments. This challenge has been addressed by many members of the Surface Science community by directing their attention to the solid/liquid interface and to biological and biomaterial interfaces. In my presentation, I will discuss some recent examples of a successful transfer of traditional Surface Science concepts to the solid/liquid interface, and of new research areas at the intersection of physics, chemistry, and biology with impact on life science and medical procedures. The need for better experimental and theoretical tools to describe solid/liquid and biological interfaces will be discussed.

9:00am **SS3-MoM3 Probing Interaction Potentials Between Surfaces in Water***, **J.G. Kushmerick**, B.C. Bunker,* Sandia National Laboratories

Adsorbed water layers are known to strongly mediate interactions between non-ionic surfaces. These so-called hydration forces control processes as diverse as protein folding and the undesired adhesion between hydrophobic surfaces in micromachine components. Until recently, most investigations of hydrophobic interactions have been performed using the surface forces apparatus and atomic force microscopy. The former technique is limited to investigations on extended mica surfaces, while the latter technique is limited to probing only the outer regions of force-distance profiles due to "snap-to-contact" problems. The difficulties associated with making localized measurements of the hydration force have now been overcome using an interfacial force microscope (IFM), which allows force-distance profiles to be obtained at sub-nanometer resolution until the tip and surface are in intimate contact. Experiments have been performed in humid atmospheres and under water. Examples of IFM investigations of hydration interactions are provided for a range of hydrophobic-hydrophilic tip-substrate combinations prepared using functionalized self-assembled monolayers (SAMS). Investigations have also been performed on SAM coatings used to control stiction in micromachines and on polymeric coatings such as poly n-isopropyl acrylamide that can be switched between hydrophilic and hydrophobic states. Results on the polymers indicate that adhesive interactions can be modified by at least an order of magnitude by conformation changes associated with the adsorption and desorption of water. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract DE-ACO4-94Al85000.

9:20am **SS3-MoM4 Determination of Molecular Structure at Polymer Interfaces by Sum-Frequency Generation***, **K.A. Briggman**, L.J. Richter, J.C. Stephenson, W.E. Wallace,* National Institute of Standards and Technology

The structure of polymer surfaces and interfaces can determine critical interfacial properties such as adhesion, molecular recognition and bonding in applications as diverse as optoelectronics and biomaterials. Linear vibrational spectroscopies (FTIR, ATIR, and Raman) are some of the most widely accepted and utilized diagnostics of bulk polymer systems but typically do not have sufficient specificity to probe interfaces. Vibrationally resolved sum-frequency generation (SFG), a non-linear optical technique, is uniquely interface specific as it is dipole forbidden in media with inversion symmetry. Additionally it has the ability to determine not only the alignment of molecular groups, but also their absolute orientation. We report vibrational SFG studies of the methylene and phenyl groups at the interfaces of thin, annealed polystyrene films. When applied to thin film systems, the contributions from multiple interfaces must be properly assigned. Multilayer systems are designed to separate the contribution of signals from the free surface and buried interface and to allow independent determinations of molecular orientation at each interface. The phenyl rings have polar order at the free surface and oriented away from the film. The degree of order is significantly weaker at the buried interface. We will present a detailed analysis of the orientational distibution of the rings.

9:40am **SS3-MoM5 Nanocrystal Surface Melting -- A UHV X-ray Diffraction Study on n-Pb***, **K.F. Peters**,* Northwestern University, FRANCE*; Y.-W. Chung,* Northwestern University

Discovery of a nanocrystal surface phase transition is reported. The surface influence on the melting of nanoparticles has been debated since seminal concepts of surface melting and of a size-dependent melting temperature were given by Faraday and Thompson. On macroscopic Pb crystals, surface melting occurs on certain surface orientations yet not others. On highly curved surfaces of nanoparticles, 3 competing melting theories are based on liquid skin formation before melting, during melting, or never. Each theory also predicts a depression of the melting temperature Tm(D) as a function of crystallite diameter D. To measure the surface melting and melting temperature of Pb nanocrystals, we applied x-ray powder diffraction in situ in UHV.@footnote 1,2@ An array of Pb nanoparticle islands of 5-50 nm diameter was fabricated on a silica substrate by evaporation and annealing. The Pb 111/200 powder diffraction peaks were collected versus temperature. Narrowing of the diffraction peak revealed the melting of smaller particles at lower temperatures. Fourier analysis of the peak shape shows the evolution of the size distribution of 'crystallites' with increasing temperature. The size-dependent melting temperature was found to be Tm(D)=1-0.62/D, in close agreement with the Liquid Skin Melting Model. To measure directly the liquid skin growth on the crystallites, we rely on the undercooling of liquid particles without solidification. First the sample is heated to within 3K of the melting temperature of the largest particles in the sample (to melt the smaller particles). Upon slight cooling, we observed a reversible increase in the diffraction intensity and a narrowing of the diffraction peak shape. These changes in the crystallite volume and size are due to small changes in the liquid skin thickness (up to 0.5nm over a 20K temperature excursion for crystallites of 20 and 50nm diameter). @FootnoteText@ @footnote 1@Appl.Phys.Lett., 71 (16), 1997, 2391-2393. @footnote 2@Phys.Rev.B, 57, 21, 1998, 13430-13438.

10:00am **SS3-MoM6 How to Study a High-Vapor Pressure Liquid under Ultrahigh Vacuum: Organic Chemistry at and near the Surface of Sulfuric Acid***, **J.T. Roberts**, R. Michelsen,* University of Minnesota

10:20am **SS3-MoM7 Atomic Structure of Sulfide Natural Crystal Surfaces by Combined Photoelectron Imaging and Diffraction Methods***, E.M. Kneedler,* Surface/Interface Inc.*; X. Chen, S. Banerjee,* University of Wisconsin, Milwaukee*; E. Rotenberg,* Lawrence Berkeley National Laboratory*; **B.P. Tonner**,* University of Central Florida

Natural surfaces of minerals play an important role in the chemistry of the environment. Advances in the sophistication of surface structural techniques makes it possible to tackle an atomic structure determination of such surfaces with some degree of confidence. We have studied a number of sulfur bearing mineral surfaces using high resolution x-ray photoelectron diffraction, and x-ray photoemission microscopy. A model system with a large unit cell, Cu(100)-S, is a starting point for evaluating the accuracy of photoelectron diffraction methods on complex surfaces. Results are also

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[1] **Featured Speaker - Science and Technology in the 21st Century**

presented for natural crystals of galena (PbS), pyrite (iron sulfide), and some preliminary results of chalcopyrite.

10:40am **SS3-MoM8 DNA Sequence Information Obtained by TOF-SIMS Analysis*, K.F. Willey*,** *W.L.B. White, T.J. Whitaker,* Atom Sciences, Inc.

A high-speed DNA screening technology is currently being developed at Atom Sciences. Our approach utilizes gene chip technology, which has paved the way for widespread DNA diagnostics. Current technology utilizes DNA hybridization to complementary oligonucleotides of known sequence immobilized to a surface. Unknown DNA is typically labeled with radioisotopes, stable isotopes, or fluorescent tags in order to detect hybridization sites. This labeling is costly and can be an impediment to the widespread use of gene chips. We are developing a new technology that requires no labeling. In this technique, target DNA hybridizes to an array of known sequences of peptide nucleic acid (PNA) probes attached to a silicon substrate. The naturally occurring phosphate groups in DNA provide an ideal intrinsic label because PNA contains no phosphorous. PNA is an analog of DNA in which the sugar/phosphate backbone of DNA is replaced by a peptide backbone. Target DNA and PNA probes undergo hydrogen bonding of AT and GC base pairs (Watson-Crick rules). Diagnostic information is obtained by identifying DNA hybridization sites within the array using negative SIMS detection of phosphate fragments. The sensitivity of SIMS detection and use of PNA probes gives our technology distinct advantages over existing diagnostic techniques (e.g. fluorescence). The major drawback, however, is the cost of commercial SIMS instrumentation. Therefore, at Atom Sciences, we have developed an inexpensive TOF-SIMS instrument. We will discuss the advantages of using a DNA/PNA hybridization scheme and its application to identifying single base mismatches. We will also discuss the current SIMS instrument used for technology development and how it could be simplified for a clinical diagnostic setting.

Thin Films

Room 203 - Session TF-MoM

Atomic Layer Chemical Vapor Deposition I

Moderator: S.M. George, University of Colorado

8:20am **TF-MoM1 Atomic Layer Deposition of Microelectronic Materials: The Present Status and Future Challenges*, M.K. Ritala,*** University of Helsinki, Finland **INVITED**

As the evolution towards increasing integration densities continues in the integrated circuit manufacturing, new materials and thin film deposition methods will inevitably be needed. Atomic Layer Deposition (ALD) is one of the most promising film deposition techniques capable of meeting the strict requirements in future generation IC manufacturing. The self-limiting film growth mechanism of ALD ensures excellent conformality and uniformity over large areas, and atomic level composition and thickness control. In this paper, the present state of ALD of materials of an interest to microelectronics will be reviewed, including also the current understanding of the related chemistry, and challenges for the future research will be outlined. At present, there already exist many potential ALD processes for the following microelectronic materials: dielectrics (e.g. SrTiO@sub 3@, BaTiO@sub 3@, Ta@sub 2@O@sub 5@, Nb@sub 2@O@sub5@, ZrO@sub 2@, HfO@sub 2@ and Al@sub 2@O@sub 3@, and their multilayers and mixtures) for gate oxides and DRAM capacitors, and nitride (e.g. TiN, TaN, NbN, W@sub 2@N) diffusion barriers for metallizations. In addition, some metal (W, Ti, Ta, Cu) ALD processes have been reported as well. Further development of ALD will require increasing efforts in precursor chemistry supported by improved understanding of the growth mechanisms. For the latter, different approaches may be taken. Here a recently developed ALD-QMS-QCM setup enabling in situ characterization of ALD processes under the practically important flow type reactor conditions will be briefly introduced.

9:00am **TF-MoM3 Atomic Layer Deposition of BN Using Sequential Exposures of BCl@sub 3@ and NH@sub 3@*, J.D. Ferguson*,** *S.J. Ferro, S.M. George,* University of Colorado

BN is an inert insulating material with a very high thermal conductivity that is desirable for many applications. Atomic layer deposition (ALD) is a useful method for growing ultrathin and conformal films. BN ALD was accomplished by separating the binary reaction BCl@sub 3@ + NH@sub 3@ --> BN + 3 HCl into two half-reactions: A) BNH* + BCl@sub 3@ --> BNBCl@sub 2@* + HCl; B) BCl* + NH@sub 3@ --> BNH@sub 2@* + HCl. BN films were grown on high surface area SiO@sub 2@ particles using alternating exposures of BCl@sub 3@ and NH@sub 3@ at 700 K. The sequential surface chemistry was monitored in a vacuum chamber using in situ transmission Fourier transform infrared (FTIR) vibrational spectroscopy. The initial SiO@sub 2@ surface contained SiOH* surface species. The first BCl@sub 3@ exposure reacted with the SiOH* species to form SiOBCl@sub x@* species. The subsequent NH@sub 3@ exposure converted the surface species to BNH@sub 2@*. The following BCl@sub 3@ and NH@sub 3@ exposures converted the surface to BCl@sub x@* and BNH@sub 2@* species, respectively. By repeating the sequential surface reactions, BN bulk vibrational modes on the SiO@sub 2@ particles increased versus number of AB cycles. In addition, spectroscopic ellipsometry studies of BN ALD on Si(100) measured BN growth rates of ~2.5 Å per AB cycle. Transmission electron microscopy also examined the conformality of the BN films on the SiO@sub 2@ particles.

9:20am **TF-MoM4 Thermal Stability of Si and C Atomic Layers Formed on Ge(100) in Silane and Methylsilane Reactions*, M. Fujiu*,** *M. Sakuraba, T. Matsuura, J. Murota,* Tohoku University, Japan

In order to realize an atomic layer superlattice of group IV semiconductors, self-limited control of adsorption and reaction of reactant gases and suppression of the mutual diffusion at the hetero interfaces are essential. In this work, thermal stability of Si and C atomic layers formed on Ge(100) in SiH@sub 4@ and CH@sub 3@SiH@sub 3@ reactions was investigated using XPS by an ultraclean low-pressure CVD system. With CH@sub 3@SiH@sub 3@ reaction on Ge(100) at 18Pa, the concentration of Si deposited on Ge(100) was nearly the same as that of C during the reaction at the temperature of 550@super o@C or lower. Especially at 450@super o@C, single atomic layers of Si and C were formed self-limitedly on Ge(100). When the single atomic layers were subsequently annealed for 60 min at 600@super o@C, the C atom concentration decreased from the single atomic layer to about half of the atomic layer, although the Si atom concentration hardly changed. The result suggests that the Si-C bond is gradually broken by annealing at 600@super o@C, and the C atom desorbs. On the other hand, with SiH@sub 4@ exposure on Ge(100) at 120Pa, the deposited Si concentration saturated to that of the single atomic layer at 300@super o@C. After formation of the Si single atomic layer on Ge(100) followed by further annealing for 60 min at 500@super o@C and subsequent SiH@sub 4@ exposure for 30 min at 300@super o@C, the deposited Si concentration increased and reached to 120% of the Si single atomic layer. It is suggested that atomic order mixing occurs even at 500@super o@C at the interface between the Si atomic layer and the Ge substrate, and the segregated Ge atom enhances the further SiH@sub 4@ reaction on the surface. The above results reveal that the atomic order mixing is greatly suppressed by the existence of C atoms on the surface. The dependence of the growth and annealing temperatures on the thermal stability of Si and C atomic layers on Ge(100) will be presented.

9:40am **TF-MoM5 Selective Growth of ZnO Thin Film on Microprinted Si Substrate***, M. Yan,* ***R.P.H. Chang****, J. Ni, J.R. Babcock, T.J. Marks,* Northwestern University **INVITED**

ZnO is an inexpensive transparent conductive material that has already received intensive studies. Recently, its interesting optical property has made it a potential LED material. Various techniques, including chemical vapor deposition (CVD), sputtering, pulse laser deposition (PLD) and atomic layer epitaxy (ALE), have been used to deposit ZnO thin film onto different substrates. In order to make devices, patterned ZnO film has to be achieved. Typically, features can be fabricated using photolithography. For mass production, however, a low cost and high throughput method is needed. In this research, ZnO thin film was deposited onto microprinted Si substrate using ALE. 1-trichlorosilyl-docosane(CH@sub 3@(CH@sub 2@)@sub 21@SiCl@sub 3@) and perfluorodecyl-1H,1H,2H,2H-trichlorosilane(CF@sub 3@(CF@sub 2@)@sub 7@CH@sub 2@CH@sub 2@SiCl@sub 3@), both of which have a long hydrophobic alkyl chain, were used as ink in microprinting. The -SiCl@sub 3@ group in the above compounds can react with the -OH groups on the surface of Si substrate, thus the hydrophobic chain was fixed on the surface of Si. Water and diethylzinc (DetZn) were used as precursors in ALE. Since water can not stick to the areas that have been covered with ink, selective growth of ZnO can be achieved. Preliminary study shows that selective growth of ZnO has been realized on microprinted Si substrates, which has feature size of 50ï�-m. Optical and Scanning Electronic Microscopy (SEM) observations show that features have satisfactory sharpness. Discussion of low temperature ALE of ZnO on different substrate, such as glass and flexible polyethylene terephthalate (PET), will be reported.

10:20am **TF-MoM7 Electrical Characterization of Ultrathin Al@sub 2@O@sub 3@ Films Grown by Atomic Layer Deposition in a Viscous Flow Reactor***, **M.D. Groner,** J.W. Elam, S.M. George,* University of Colorado

Al@sub 2@O@sub 3@ is an important insulator and is a candidate to replace SiO@sub 2@ as a gate dielectric in MOSFETS. Al@sub 2@O@sub 3@ films were deposited by atomic layer deposition (ALD) using alternating exposures of trimethylaluminum and H@sub 2@O on a variety of substrates. The films were grown in a custom viscous flow reactor employing a novel gas pulse switching method. The film growth was monitored in situ by a quartz microbalance and ex situ using ellipsometry. The electrical properties of the A l@sub 2@O@sub 3@ films were evaluated by performing I-V and C-V measurements with a mercury microprobe. The highest quality ALD Al@sub 2@O@sub 3@ films were obtained using ultraclean Si(100) substrates or molybdenum substrates. The ALD Al@sub 2@O@sub 3@ films exhibited extremely low leakage current levels. The electrical properties of the ALD Al@sub 2@O@sub 3@ films deposited on molybdenum were examined versus Al@sub 2@O@sub 3@ thickness from 30 Å to 2400 Å. The C-V measurements revealed that the dielectric constant was k=7.8 for Al@sub 2@O@sub 3@ films @>=@ 1200 Å. The dielectric constant decreased below 100 Å to k=4.0 at 25 Å. The I-V measurements showed that the Fowler-Nordheim (FN) tunneling onset voltage decreased with Al@sub 2@O@sub 3@ film thickness. The onset of FN tunneling occurred at >10 V for 600 Å films and at ~3.5 V for 60 Å Al@sub 2@O@sub 3@ films.

10:40am **TF-MoM8 A Study on the Characteristics of TiAlN Thin Film Deposited by Atomic Layer Chemical Vapor Deposition Method***, **H. Jeon,** J.W. Lee, J.H. Koo, T.H. Doh, Y.D. Kim,* Hanyang University, South Korea

Atomic Layer Chemical Vapor Deposition(ALCVD) method is one of the new deposition method to grow very thin films.@footnote 1@ Conventional PVD and CVD methods exhibit problems such as poor step coverage, impurity contamination and particle generation. ALCVD method has a lot of advantages over other CVD processes and these are excellent thickness uniformity, conformal step coverage, very low pinhole density, and complete elimination of particle generation by gas phase reaction.@footnote 2@ The sequential control of the growth in ALCVD system is based on saturating surface reactions between the substrate and each of the reactant needed for the compound to be grown. Each surface reaction adds full or partial fraction of monolayer of the material on the surface. Here we deposited TiAlN ternary diffusion barrier by ALCVD method. Ternary diffusion barrier is considered to be more efficient than binary diffusion barrier such as TiN. But ternary film of Ti-Si-N has high resistivity to apply for actual process. In this study we deposited TiAlN ternary diffusion barrier to study the diffusion barrier characteristics.@footnote 3@ TiCl@sub 4@ vapor, DMAH-EPP vapor, and NH@sub 3@ gas were alternatively introduced into reactor to form TiAlN by ALCVD. The physical and chemical properties of TiAlN films were analized by TEM, AES, RBS, and SEM. The growth mechanism will be discussed based on the results of characteristics of TiAlN. @FootnoteText@ @footnote 1@T. Suntola, Thin Solid Films, 216, 84-89(1992) @foontote 2@S. Yokoyama, H. Goto, T. Miyamoto, N. Ikeda, K. Shibahara, Applied Surface Science, 112, 75-81(1997) @footnote 3@ C. W. Kim, K. H. Kim, Thin Solid Films, 307, 113-119(1997).

Biomaterial Interfaces
Room 202 - Session BI+MC-MoA

Characterization of Biomaterial Interfaces

Moderator: L. Hanley, University of Illinois at Chicago

2:00pm **BI+MC-MoA1 Surface Tools for the Characterisation of Biomaterials***, **M.C. Davies**, S.J.B. Tendler, C.J. Roberts, P.M. Williams, S. Allen,* University of Nottingham, UK **INVITED**

Understanding the interfacial chemistry of biomaterials has long been a goal in the search for optimum biocompatibility. The interfacial environment has a major control on materials properties and the exploitation of nanosurface engineering, to tailor the optimum surface behaviour and function has made a significant impact in the biotechnological and biomedical sciences over the last decade. This talk will explore the role of advanced surface tools for the characterisation of modern biomaterial materials and review the limitations and advantages of different approaches, highlighting fruitful areas for future activity.

2:40pm **BI+MC-MoA3 Electrochemical SPR for Biomaterial Applications***, **R.M. Georgiadis**,* Boston University, usa*; R.J. Heaton,* Boston University

Electrochemical SPR is the combination two powerful surface specific techniques which together provide the basis for many surface modification and detection schemes with new applications to biomaterial interfaces. Although the general effect of an applied electrochemical potential on the surface plasmon resonance response from a simple metal surface is well known, the response from more complex interfaces has not been studied in detail. Yet, such studies are crucial for many applications such as quantifying binding at interfaces in the presence of an applied electrochemical field. We show that very useful information can be obtained directly from the potential dependent SPR optical data: the potential of zero charge can be determined in the presence or absence of immobilized organic or biomaterial films and the specific adsorption of anions can also be distinguished. We report results for a series of modified interfaces including self assembled monolayer films and for thiol bound DNA oligomer films in various electrolytes.

3:00pm **BI+MC-MoA4 Characterization of Surface Modified Microporous PTFE Biomembranes using Surface Charge, Topography and Chemistry Studies***, **I.D. Baikie**, B. Lägel,* Robert Gordon University, UK

Functionalised microporous PTFE membranes have many applications involving cell growth and adhesion such as skin grafting and cell scaffolds. Key factors in promoting cell growth are the chemistry and topography of the surface, however a much overlooked surface parameter is that of surface charge. Using a multitip scanning kelvin probe (SKP)@footnote 1@ we have performed surface potential/charge topographies of bare and surface modified bio-membranes prior to Human Skin Fibroblast growth. Additionally surface characterization with SEM and XPS provided topography and chemistry information on the top-most layers. Subsequent video-microscopy growth data indicates an extraordinary correlation between a regime of homogeneous negative surface charge profiles and confluent HSF films. Indeed the optimum growth surface displays two dimensional charge transport characteristics. Up to now little work has been performed on the electrical properties of modified polymers due to the difficulties in obtaining accurate surface potential data. The SKP features a truly noninvasive charge imaging measurement mode and we anticipate many future applications both in monitoring biomaterials and biological interfaces. @FootnoteText@ @footnote 1@I. Baikie, P.J.S. Smith, D.M. Porterfield and P.J. Estrup, Rev. Sci. Instrum. 70, 1842 (1999).

3:20pm **BI+MC-MoA5 Enhanced TOF-SIMS Imaging of a Micropatterned Protein by Stable Isotope Protein Labeling***, **A. Chilkoti**,* Duke University*; A. Belu,* Physical Electronics*; Z.P. Yang,* Imation Inc.*; R. Aslami,* Duke University

Patterning of biomolecules on surfaces is an increasingly important technological goal. Because the fabrication of biomolecule arrays often involves step-wise, spatially resolved derivatization of surfaces, spectroscopic imaging of these arrays is important in their fabrication and optimization. Although imaging time-of-flight secondary ion mass spectrometry (TOF-SIMS) is a powerful method for spatially resolved surface analysis of organic molecules on surfaces, TOF-SIMS images of micropatterned proteins on organic substrates can be difficult to acquire because of the lack of high intensity, protein specific molecular ions that are essential for imaging under static conditions. In contrast, low mass ions are of suitable intensity for imaging, but can originate from different chemical species on the surface. A potential solution to this problem is utilize stable-isotope labeled proteins, an approach that has heretofore not been explored in TOF-SIMS imaging of micropatterned proteins and peptides. In order to investigate the feasibility of stable isotope enhanced TOF-SIMS imaging of proteins, we synthesized @super 15@N-labeled streptavidin by metabolic labeling of the protein during expression from a recombinant gene. The spatial distribution of streptavidin bound to biotin micropatterns, fabricated on a polymer and on a self-assembled monolayer on gold, was imaged by TOF-SIMS. Imaging of high intensity, low m/z secondary ions (e.g., C@super 15@N@super -@ and C@super 15@NO@super -@) unique to streptavidin, enabled unambiguous spatial mapping of the micropatterned protein with a lateral resolution of a few microns. TOF-SIMS imaging of micropatterned @super 15@N-labeled streptavidin also illustrated the exquisite sensitivity of TOF-SIMS to low fractional coverage of protein (0.5 nm effective thickness) in the background regions of the protein micropattern.

3:40pm **BI+MC-MoA6 Quantitative Chemical Mapping of Lipid-protein Langmuir-Blodgett Layers by Laser-SNMS***, **N. Bourdos**, F. Kollmer, R. Kamischke, H.-J. Galla, A. Benninghoven,* Westfälische Wilhelms-Universität, Germany

Quantitative molecular mapping of chemically modified or functionalized surfaces is still an important challenge in surface analysis. We demonstrate that analyzing sputtered neutrals may be a big step forward in the quantitative mapping of laterally structured overlayers of organic molecules or biomolecules, respectively. We studied samples consisting of phospholipids and a small 34-residue peptide, the surfactant protein C (SP-C). These overlayers are phase-separated into a fluid and condensed phase. They were prepared on Au substrates with the Langmuir-Blodgett (LB) technique and investigated using a combined SIMS/SNMS instrument equipped with a reflectron-type TOF analyzer, a 30 keV Ga+ primary ion source, and an excimer laser for resonantly enhanced multiphoton post-ionization of neutrals. Laser-SNMS was applied for the first time to study LB layers. The SP-C clearly engenders typical amino acid-specific neutral fragments, by which it can be identified and localized on a surface. Most of them result from the cleavage of the COOH group, e. g., CH@sub4@N, C@sub 4@H@sub 8@N or C@sub 5@H@sub 12@N. The small CN is not typical of a certain amino acid but the entire molecule. It is the most intense peptide-based secondary particle and therefore gives excellent maps of SP-C-rich domains formed in the overlayer. It is possible to calculate the protein content in a lipid layer by histogram evaluation. The yields and damage cross-sections calculated from TOF-SIMS measurents indicate that the lateral resolution may be far below instrument limitations (beam focus). A quantitative comparison of the secondary particle emission from SP-C-rich and SP-C-free domains (on the same substrate) allowed some insight into the process of secondary ion and neutral generation from the molecular overlayer as well as from the substrate.

4:00pm **BI+MC-MoA7 Probing the Spatial Organization of Mixed Lipopeptide/Phospholipid Monolayers : Complementarity of AFM and XPS***, **Y.F. Dufrene**,* Universite Catholique de Louvain, Belgium*; M. Deleu, P. Jacques,* Faculte Universitaire des Sciences Agronomiques de Gembloux, Belgium*; P. Thonart,* Centre Wallon de Biologie Industrielle, Belgium*; M. Paquot,* Faculte Universitaire des Sciences Agronomiques de Gembloux, Belgium

Surfactin is a surface-active bacterial lipopeptide, with important biological properties, which is known to interact with lipid membranes. To gain insight into the spatial organization (miscibility, molecular orientation) of mixed surfactin/dipalmitoyl phosphatidylcholine (DPPC) monolayers, the morphology and chemical composition of mixed monolayers transferred on mica were determined by atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS), respectively. AFM topographic and friction images revealed phase-separation for mixed monolayers prepared at 0.1, 0.25 and 0.5 surfactin molar ratios. The step height measured between the surfactin and the DPPC domains was about 1.2 nm, pointing to a difference in molecular orientation: while DPPC had a vertical orientation, the large peptide ring of surfactin was lying on the mica surface. These data were in excellent agreement with the monolayer properties at the air-water interface and with computer simulation data. The N/C atom concentration ratios obtained by XPS for pure monolayers were consistent with two distinct geometric models: a random layer for surfactin and for DPPC, a layer of vertically-oriented molecules in which the polar headgroups are in contact with mica. XPS data for mixed systems were accounted for by a combination of the two pure monolayers, considering respective surface coverages that were in excellent agreement with those measured by AFM. Finally, exciting new possibilities offered by dynamic AFM imaging modes (force modulation, phase imaging) to investigate the film nanomechanical properties will be presented. This work demonstrates the complementarity of AFM imaging and XPS analysis to directly probe the molecular organization of multicomponent monolayers.

4:20pm **BI+MC-MoA8 Detection of Intact Biomolecules with Matrix-Enhanced ToF-SIMS***, **D.G. Castner**, P. Kingshott, J. Nesiba, S.L. Golledge, B.D. Ratner,* University of Washington

An improved understanding of the interfacial interactions between biomolecules and surfaces is important for the successful design of the next generation of biomaterials. This study combines the high surface sensitivity and chemical specificity of ToF-SIMS with the 'soft' ionization capabilities of MALDI. Model peptides with beta-sheet and alpha-helix structures were used in conjunction with MALDI matrix molecules [2,5-dihydroxybenzoic acid (DHB) and sinapinic acid (SA)] to facilitate generation of molecular ions with the SIMS Cs+ ion source. The positive ToF-SIMS spectra from the beta-sheet peptide incorporated into crystals of DHB show peaks representative of sodium-adduct ions of the peptide (M-H+Na+) (m/z 1096.7). The spectrum from the bulk beta-sheet contains only fragment ions and no molecular ions, suggesting that there is a synergistic effect in producing sodium adduct molecular ions when both Na and matrix molecules are present. When sodium is eliminated from the system, peaks that can be assigned to the M+ ion (m/z 1074.7) can still be detected. Molecular ions from the alpha-helix peptide were also detected when DHB was present. The use of SA as matrix failed to generate peptide molecular ions, suggesting the matrix-specific nature of this MALDI-SIMS technique. Imaging-SIMS indicated that the peptides are incorporated within the DHB matrix crystals, but are not fully incorporated into the SA crystals. This shows the importance of good mixing between the peptides and matrix molecules for detection of intact molecular ions.

4:40pm **BI+MC-MoA9 Molecular Orientation of Annealed Artificial Joint Polymers: Characterization by Soft X-ray Absorption***, S. Sambasivan,* SUNY Stony Brook*; **D.A. Fischer**,* National Institute of Standards and Technology*; M. Shen,* University of Maryland*; J.A. Tesk, S. Hsu,* National Institute of Standards and Technology

For the past 30 years ultra-high molecular weight polyethylene (UHMWPE) has remained the dominant polymer in artificial joints due to its outstanding wear resistance properties. It has been recognized that wear of UHMWPE contributes to the loosening of the implants and is the main cause for the failure of long-term implants. Hence, there is an urgent need to understand the mechanism and the surface morphology leading to wear and failure of the artificial joint. Hubbard et al.@footnote 1@ and Hastings et al.@footnote 2@ have demonstrated that the molding and annealing the UHMWPE at safe elevated temperatures resulted in increased mechanical strength. Also, cross-linking of UHMWPE has been demonstrated to reduce wear significantly. We have previously measured molecular orientation as a function of wear motion.@footnote 3@ Molecular orientation in biomaterials is thought to be critical in characterizing the precursors of wear and the production of debris during the wear process. While the link between molecular orientation and wear has not been clearly established, molecular orientation has been recognized as an important parameter in wear resistance. This study examines the change of molecular orientation caused by annealing UHMWPE. Our technique utilizes soft x-ray absorption spectroscopy at a synchrotron beamline to non-destructively characterize the molecular orientation of the UHMWPE surface layer. Current methods of inferring or deducing orientation are not accurate and often rely on staining and cutting specimens.@FootnoteText@ @footnote 1@Hubbard et al., Trans. 25th Soc. For Biomaterials, 325(1999). @footnote 2@Hastings et al., Trans. 25th Soc. For Biomaterials, 328(1999). @footnote 3@Fischer et al., Trans. 25th Soc. For Biomaterials, 351(1999).

5:00pm **BI+MC-MoA10 Titanium-Alginic Acid Chemistry of Adhesion Using X-ray Photoelectron Spectroscopy***, **R.A. Brizzolara**,* David Taylor Research Center, NSWC

The interfacial chemistry between alginic acid and a titanium surface has been examined using x-ray photoelectron spectroscopy (XPS). This study is motivated by the effort to mitigate effects of seawater biofouling on heat transfer surfaces via materials or surface modification strategies. Alginic acid is a predominant adhesive in bacterial biofilms, and titanium is a common material in naval ship cooling and piping systems. XPS has been used to quantify the alginic acid adsorbed to the titanium surface from aqueous solution. The experiments were performed at various solution pH's to examine the effect on alginic acid adsorption of changing the charge state of the ionizable groups on the alginic acid and of the titanium surface. The effects of ions in the solution were investigated by performing the alginic acid adsorption in the presence of calcium chloride. To separate the effects of the carboxyl and hydroxyl moieties present in alginic acid, XPS has also been used to measure caproic acid (carboxyl) and glucose (hydroxyl) adsorption as a function of solution pH. High-resolution XPS spectra have been utilized to separate the various carbon and oxygen chemistries present, and angle-resolved XPS spectra and advancing contact angle measurements were used to elucidate molecular orientation effects. Atomic force microscope (AFM) images were obtained to determine adsorbate morphology and surface coverage. These data will be interpreted in light of potential alginic acid - titanium adsorption mechanisms such as hydrogen bonding and anion exchange. This information regarding the biofilm-surface chemical interaction will be useful in developing fouling resistant surfaces. The NSWC Carderock Division In-House Laboratory Independent Research Program supported this work.

Flat Panel Displays
Room 313 - Session FP-MoA
Flexible Displays

Moderator: R.M. Wallace, University of North Texas

2:40pm **FP-MoA3 Microencapsulated Electrophoretic Particle Systems for Flexible Electronic Display Applications***, **P.S. Drzaic**,* E Ink Corporation **INVITED**

The proliferation of portable electronic devices has caused increased interest in new display technologies that overcome the many limitations in traditional flat panel displays. In particular, most current display technologies, particularly those based on fluids, require one or more sheets of glass in the display construction. One strategy for making fluid-based display technologies compatible with film substrates is to create a dispersion of a fluid in a polymer matrix. Microencapsulated electrophoretic displays@footnote 1@ ("electronic ink") offer a unique and interesting set of properties: high reflectivity and contrast, a paperlike appearance, low power consumption, and compatibility with flexible substrates. In electronic ink displays, microcapsules serve to contain a colored, nonaqueous fluid containing electrophoretically-mobile particles. An electric field is used to move particles to either the front or back of the display, so that a viewer either sees the particles or the colored oil. Depending on the surface chemistry of the colloid and polymer, the particles can remain in place long after the electric field is removed. This property gives the display image an inherent persistence of the without further power consumption. Here, I will describe the optical and electrical characteristics of these microencapsulated display materials based on rutile titanium dioxide colloidal particles. Electronic ink devices are also highly compatible with microelectronic circuits, either based on traditional silicon devices or on novel semiconducting organic materials, and I will also discuss recent progress in this integration. @FootnoteText@ @footnote 1@B. Comiskey, J.D. Albert, H. Yoshizawa, J. Jacobson, Nature, 394, 253 (1998).

3:20pm **FP-MoA5 Low Temperature Deposition and Characterization of Polycrystalline Si Films***, **S.I. Shah**, K. Xu, D. Guerin,* University of Delaware

Polycrystalline silicon (poly-Si) thin films were deposited by dc magnetron sputtering at temperatures as low as 150°C on poly(ethyleneterephthalate) (PET) and glass cover slips. Film growth was studied as a function of the partial pressures of argon, hydrogen and krypton and different substrate bias conditions. X-ray diffraction analyses showed that films grown with a gas ratio (Ar: Kr: H@sub2@ = 17:2:1) were polycrystalline. The crystallinity of the films was also dependent on the applied substrate bias. Both the dc bias and the partial pressure of Kr enhanced the adatom mobilities leading to a crystalline film formation. The substrate bias, however, had a critical limit beyond which the crystallinity of the films again decreased. X-ray photoelectron spectroscopy (XPS) depth profiles indicated intermixing at the film-substrate interface. The intermixing was strongly dependent on the ion bombardment due to the substrate bias. We will present TRIM models to explain the effects of both the H and Kr addition to the sputtering gas.

3:40pm **FP-MoA6 Ultra-Barriers of ITO with Low Sheet Resistance***, **C.I. Bright**, M.A. Roehrig,* Presstek, Inc.

The drive to develop Flat Panel Displays (FPD) on flexible substrates has been impeded by the permeability of plastic substrates to water vapor and oxygen which degrade the display medium or electrode materials.

Recently, dielectric and ITO thin films barrier layers, separated by polymer layers, vacuum deposited on plastic sheets have demonstrated oxygen and water vapor transmission rates at or below the measurement limits of commercial instrumentation (0.005 cc/m@super 2@day and 0.005 gm/m@super 2@day). We report for the first time, ITO ultra-barriers with performance at or below this measurement limit, produced by vacuum roll to roll deposition. These ITO ultra-barriers, sputter deposited on plastic film substrates, have a typical visible transmittance of > 80% and a sheet resistance of < 20 ohms/square. Details of the deposition process, multilayer construction and measured performance are reported.

4:00pm **FP-MoA7 The Incorporation of High Performance Silicon-based Devices on Flexible Substrates using Self-Orienting Fluidic Transport**, ***R. Stewart,*** Alien Technology **INVITED**

PLEASE SEND US AN ABSTRACT. Thank you.

4:40pm **FP-MoA9 Deposition of Silicon Nitride on a Polymer Substrate by Plasma Enhanced Chemical Vapor Deposition**, ***D. Guerin,*** *S.I. Shah,* University of Delaware

Silicon nitride thin films were deposited on poly(ethyleneterephthalate) (PET) by plasma-enhanced chemical-vapor deposition (PECVD) in a capacitively coupled reactor. The process of film growth was examined using X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM). Films were grown for varying lengths of time and transferred under vacuum into an attached XPS system. AFM measurements were performed ex situ. Results indicated that the film growth process was highly dependent on the power density of the plasma. The higher the power density, the longer it took to achieve a pure silicon nitride film. With higher power plasma, the etching of the polymer substrate was observed in the initial stages of the process. This provided carbon and oxygen atoms which get incorporated into the film. Power density also affects the morphology of the thin films. In lower energy plasmas, there is less chemical interaction between the substrate and deposited film. High resolution XPS measurements of the C 1s region indicated that the main effect of the plasma on the substrate was to modify the surface such that an amorphous polymer interface was created between the bi-axial crystalline polymer and the amorphous inorganic film. The little carbon that did get incorporated into the film was C-H bound. Above some critical power density a distinct carbon peak appeared indicating that carbon from the substrate is being incorporated into the film through either Si-C or N-C bonds. AFM measurements revealed that higher energy deposition led to higher nucleation density and surface coverage. XPS measurements, however, continued to show the C 1s peak even after 40 sec. of deposition. In samples deposited at low energy, the C 1s peak disappeared after only 30 sec. of deposition. Based on these observations, we will present a model of the initial stages of silicon nitride growth on PET.

5:00pm **FP-MoA10 Mechanical Properties and Thin Film Transistor Performance for Flexible Displays**, ***S. Wagner,*** *H. Gleskova, Z. Suo,* Princeton University

Flexible displays have become of considerable near-term interest for portable computing and communication devices, because flexibility is equated with ruggedness and light weight. In these applications the displays may be flexed only a few times before they become permanently embedded, often in nonplanar configurations. Longer-term applications include products that will be flexed throughout their entire lives, for example, rollable displays and electronic books. While in some instances display components may be deformed plastically during fabrication, one may seek to exclude plastic deformation during use. Elastic deformation may be induced by bending, coiling, twisting, or stretching. We will focus on the best-understood case of elastic deformation by bending. Three question arise when a thin film transistor (TFT) is subjected to bending: (i) How much bending can a TFT tolerate? (ii) What happens in the TFT during bending? (iii) How does fatigue from repeated bending manifest itself? We have found that: (a) We are beginning to understand elastic deformation of TFT/substrate structures, but still need to understand plastic deformation; (b) Amorphous silicon TFTs are more sensitive to tensile than to compressive strain, and surface passivation may make them more resistant against tensile failure; (c) The mechanical properties of substrate and encapsulation should be tuned such that the circuit comes to lie in the neutral plane.

Magnetic Interfaces and Nanostructures
Room 206 - Session MI-MoA

Thin Films and Multilayers

Moderator: D.P. Pappas, National Institute of Standards and Technology, Boulder

2:00pm **MI-MoA1 Positive Exchange Bias Model: Fe/FeF@sub 2@ and Fe/MnF@sub 2@ Bilayers**, *M. Kiwi, J. Mejía-López,* Pontificia Universidad Católica, Chile*;* ***R.D. Portugal***[1], Pontificia Universidad Católica, Chile, France*; R. Ramírez,* Pontificia Universidad Católica, Chile

Positive exchange bias (PEB) is a phenomenon that was recently observed experimentally while normal (or negative) exchange bias (NEB) had been discovered more than forty years ago. It is remarkable that both phenomena are observed in the same samples subject to different cooling fields. Here we put forward a model to explain PEB and its crossover to NEB in Fe/FeF@sub 2@ and Fe/MnF@sub 2@ bilayers. Our model incorporates recent experimental information, such as the perpendicular coupling between the ferromagnet (FM) and the antiferromagnet (AFM) and that compensated AFM interfaces show the highest NEB shifts. A freezing of the canted AFM interface spins is proposed, and thus while hysteresis loops are performed the energy is stored in an incomplete domain wall in the FM. Recent polarized neutron reflectometry experiments provide strong support for this picture.@footnote 1@ The energy minima at each point of the magnetization curve are obtained exactly, with arbitrary precision, by a new analytical formulation which is introduced in this work. The results extracted from the model are in qualitative and quantitative agreement with available experimental facts. @FootnoteText@ @footnote 1@ M R Fitzsimmons et al., Phys. Rev. Lett. 84, 3986 (2000).

2:20pm **MI-MoA2 Asymetry of Magnetization Reversal in the Fe/(Fe,Mn)F@sub 2@ Exchange Bias System as a Function of Crystallinity**, ***A. Hoffmann,*** *M.R. Fitzsimmons,* Los Alamos National Laboratory*; C. Leighton, K. Liu, I.K. Schuller,* University of California, San Diego*; J. Nogués,* Universitat Autònoma de Barcelona, Spain*; C.F. Majkrzak, J.A. Dura,* National Institute of Standards and Technology*; H. Fritzsche,* Hahn-Meitner Institut, Berlin, Germany

Using polarized neutron reflectometry we have recently shown that the magnetization reversal can be different on both sides of the hysteresis loop for polycrystalline Fe exchange coupled to epitaxial twinned FeF@sub 2@ or MnF@sub 2@.@footnote 1@ Namely, with decreasing field (+M@sub s@ -> -M@sub s@) we observe a rotation of the magnetization indicated by the presence of spin-flip scattering, while for increasing field (-M@sub s@ -> +M@sub s@) the data suggest magnetization reversal by domain wall motion. However for epitaxial twinned films of FeF@sub 2@ and MnF@sub 2@, this difference of magnetization reversal depends on the direction of the cooling field with respect to the crystallographic orientation. In order to clarify the role of frustration between twinned antiferromagnetic domains, we examined the asymmetry of the magnetization reversal also in samples with either single-crystal (untwinned) or (110) textured polycrystalline FeF@sub 2@ films. In untwinned and textured samples we detected no significant asymmetry in the magnetization reversal. This suggests that the twinning of the antiferromagnet is essential for the asymmetry in the magnetization reversal to occur. This can be understood by a "45 degree coupling" of the Fe to the FeF@sub 2@ due to a twin-driven frustration. As a result there can be a unidirectional anisotropy due to exchange bias along the easy axis of the ferromagnet, which in turn then may give rise to the asymmetry in the magnetization reversal. This work was supported by U.S. Department of Energy, BES-DMS under Contract No. W-7405-Eng-36, grant DE-FG03-87ER-45332, and funds from the University of California Collaborative University and Laboratory Assisted Research. @FootnoteText@ @footnote 1@ M.R. Fitzsimmons, P. Yashar, C. Leighton, I.K. Schuller, J. Nogués, C.F. Maikrzak, and J.A. Dura, Phys. Rev. Lett. vol. 84, 3986 (2000).

2:40pm **MI-MoA3 Growth and Magnetic Properties of Ultrathin Fe on Pd(110)@footnote 1@**, *B. Roldan Cuenya, J. Pearson, C. Yu,* ***D. Li,*** *S.D. Bader,* Argonne National Laboratory

While it is known that initial metal growth on Pd(110) surfaces is highly anisotropic and tends to form nanoscale wires, the magnetic properties of such systems are less studied. We have investigated the growth and magnetic properties of 0-3 ML Fe on a stepped Pd(110) with SMOKE, RHEED, and LEED in order to address the correlation among morphology, structure, and magnetic properties at low dimensions. The Fe films, grown

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[1] **Falicov Student Award Finalist**

at 70 °C, are flat and epitaxial up to 1.5 ML, where 3-dimensional growth starts. RHEED oscillations with 1-ML period were observed on the (1,0) and (2,0) streaks while an oscillation with a period of 0.5-ML exists on the (0,0) streak. The initial growth is pseudomorphic. The in-plane row spacing along the [110] direction starts to relax at ~ 0.5 ML and decreases by ~ 5% at 3 ML. The submonolayer Fe films remain ferromagnetic down to ~ 0.35 ML, below which the Curie temperature (T@sub C@) may become lower than our low-temperature limit of 25K. The T@sub C@ initially increases sharply with coverage and starts to saturate at 0.8-1 ML to ~210K. The magnetic easy axis is perpendicular to the surface for 0.4-0.7ML of Fe and in-plane for Fe thicknesses > 2 ML. Between 0.7-1.2 ML, there appear to be mixed magnetic phases as indicated by the co-existence of both polar and longitudinal Kerr signals, and an increase in coercivity. @FootnoteText@ @footnote 1@ Supported by DOE BES-MS #W-31-109-ENG-38 and ANL LDRD#00-001N. @footnote 2@ J.-P, Bucher, E. Hahn, P. Fernandez, C. Massobrio, and K. Kern, Europhysics Lett., 27, 473 (1994).

3:00pm **MI-MoA4 Real Space Study of Ultrathin Fe Films on Cu(100)***, **A. Biedermann**, M. Schmid, P. Varga,* Vienna University of Technology, Austria

Ultrathin iron films deposited on Cu(100) represent a prototype system for the exploration of novel magnetic structures and thin film magnetism. We present the first atomically resolved survey of the surface/ thin film structures using scanning tunneling microscopy (STM). The clean thin films deposited at room temperature are known to be pseudomorphic (fcc) between 2 and 10 monolayer film thickness, however, with notable deviations from the ideal structure. We have identified (1) a novel "striped-bcc" phase at 4-5 monolayer film thickness and (2) the structure of the initial bcc grains at 6-8 monolayer film thickness. Locally, both the "striped-bcc" phase and the initial bcc-Fe grains show a strained bcc configuration, identifying the tendency of the Fe films to form a bcc-lattice as a common driving force for the observed structures. The appearence of the "striped-bcc" phase coincides with an increased ferromagnetism at 4-5 monolayer thickness seen by several other groups.

3:20pm **MI-MoA5 Spin Reorientation Transition in Magnetically Coupled Fe/Cu/Ni/Cu(001) System***, **H.J. Choi**[1], W.L. Ling, J.H. Wolfe,* University of California, Berkeley*; S. Anders, A. Scholl,* Lawrence Berkeley National Laboratory*; F. Nolting, H. Ohldag,* Stanford Synchrotron Radiation Laboratory*; U. Bevensiepen, R. Kawakami, Z. Qiu,* University of California, Berkeley

It is well known that low temperature grown Fe film on Cu(001) exhibits spin reorientation transition (SRT) at a critical thickness where the magnetic remanence is greatly suppressed within a pseudo-gap region. Subsequent experiments showed that the loss of the macroscopic magnetization is due to the formation of magnetic stripe domains. It is generally believed that the understanding of the strip domains will greatly advance our knowledge on the magnetic long-range order in two-dimensional Heisenberg system. With this motivation, we investigated the SRT of Fe film in Fe/Cu/Ni/Cu(001) system where the Fe layer is magnetically coupled to the perpendicular magnetization of Ni with the interlayer coupling strength being controlled by the Cu thickness. With in situ surface magneto-optic Kerr effect measurement, we show that the Fe-Ni interlayer coupling results in an alternating alignment of the Fe magnetization with Cu thickness for Fe film thinner than the SRT thickness d@sub R@, but has no effect for Fe film thicker than d@sub R@. The SRT thickness d@sub R@, defined as the onset of in-plane magnetization, was found to be independent of the Fe-Ni interlayer coupling. Within the SRT pseudo-gap region, however, the longitudinal magnetic remanence exhibits oscillatory behavior with Cu thickness with a periodicity exactly half of that of the oscillatory interlayer coupling. This result shows that the strip domains are severely modified by the strength of the Fe-Ni interlayer coupling. To provide more detailed information, element specific domain imaging was taken in this system using photoemission electron microscope at the Advanced Light Source of Lawrence Berkeley National Laboratory.

3:40pm **MI-MoA6 Magnetic Anisotropies in Ultra-Thin Films: The Spin-Reorientation Transition in Fe(110)/W(110)***, **E. Vescovo**, H.-J. Kim,* Brookhaven National Laboratory **INVITED**

Reorientation of the easy axis of magnetization are not unusual in ultra-thin films. They are generally understood as the result of a delicate energy balance between three dimensional anisotropy terms - which favor the bulk easy-axis direction - and two-dimensional surface and interface terms - which can favor a different direction. Bulk contributions are proportional to the film thickness. Correspondingly, in thin films, there can be a critical thickness (t@sub R@) at which the two contributions balance exactly. In all those cases, a switch of the magnetization has to be expected when crossing t@sub R@. Fe(110) films epitaxially grown on W(110) display a spin reorientation phase transitions as a function of film thickness.@footnote 1@ This transition --- from the in-plane [110] direction to the [100] direction --- is characterized by a t@sub R@ of about 50 monolayers. Here we report on new spin- and angle-resolved photoemission experiments on this system. We show how t@sub R@ can be greatly varied by directly manipulating the Fe(110) surface. Furthermore, we explore the temperature dependence of the anisotropy balance and provide compelling evidence demonstrating that this in-plane spin reorientation transition can also be induced by varying the temperature, at constant thickness. @FootnoteText@ @footnote 1@ H.J. Elmers and U. Gradmann, Appl. Phys. A 51, 255 (1998)

4:20pm **MI-MoA8 Fermi Surfaces and Magnetic Behavior of Thin FeNi Alloy Films***, **M. Hochstrasser**, N.A.R. Gilman, R.F. Willis,* The Pennsylvania State University*; F.O. Schumann, J.G. Tobin,* Lawrence Livermore National Laboratory

We report angle-resolved and spin-resolved photoemission measurements of changes in the electronic structure with changing composition of pseudomorphic films of FeNi magnetic alloys grown epitaxially on Cu(100). With x-ray magnetic linear dichroism angle dependent (XMLDAD) 3p core-level photoemission the evolution of the elemental magnetic moments was monitored. In addition, changes occuring in the spin-polarized valence bands were observed with spin-polarized photoemission, together with changes in the k-distribution of states at the Fermi energy. A projection of the Fermi surface shows a delocalized "dogbone" feature due to sp-states and more localized "hotspots" corresponding to the emergence of minority spin d-states. Hybridization between the s p- and d-states occurs at thesse locations on the dogbone indicative to a strong nesting of wavevectors of excitations spanning the Fermi surface. The sp-dogbone states spin polarize with increasing average magnetic moment. Both elemental moments, observe d in XMLDAD, grow with increasing Fe concentration up to a maximum at the Fe concentration of 55%, that on the Fe increasing at a faster rate than the Ni moment. Beyond this point, the Fe moment shows a rapid decline to a "low-spin" value, of the order of that of the Ni monent, which tracks the behavior of the Fe moment but to a smaller degree. Spin-resolved valence band photoemission measurements show first an increase in the exchange splitting of 3d-states, followed by a decline, essentially tracking th e core-level dichrosim. The magnetic instability observed abovethe invar concentration (Fe > 65%) is characterized further by a diffuseness in the spectral distribution and an increased lifetime broadening of mainly minority-spin states, indicative of magnetic non-collinear disorder.

4:40pm **MI-MoA9 Highly Spin-Polarized Chromium Dioxide Thin Films Prepared by Chemical Vapor Deposition from Chromyl Chloride***, **W.J. DeSisto**,* University of Maine*; P.R. Broussard,* Covenant College*; T.F. Ambrose, B.E. Nadgorny, M.S. Osofsky,* Naval Research Laboratory

Highly spin-polarized materials, and in particular thin films, are central to many magneto-electronic devices. An efficient and controlled chemical vapor deposition (CVD) process for depositing highly spin-polarized, metastable chromium dioxide (CrO@sub 2@) on (100) TiO@sub 2@ substrates has been developed using chromyl chloride (CrO@sub 2@Cl@sub 2@) as a precursor. This precursor is a liquid at room temperature with a vapor pressure adequate for CVD using conventional precursor handling equipment. The films were shiny, black, and approximately 200 nm thick. The spin polarization, as measured by the Point Contact Andreev Reflection (PCAR) technique, was 81± 3%. X-ray diffraction @theta@/2@theta@ scans indicated the films grew completely (100) oriented, in registry with the (100) oriented TiO@sub 2@ substrate. X-ray diffraction @phi@-scans on the CrO@sub 2@ (110) reflection indicated the expected two-fold symmetry, with no evidence of misaligned material. The resistivity at room temperature was 240 @micro@@ohm@cm and decreased to 10 @micro@@ohm@cm at 5K, consistent with metallic behavior. The films were ferromagnetic with a Curie temperature of 395 K and a coercivity of approximately 100 Oe at 298 K. This deposition technique enhances the possibility of fabricating a GMR and/or a tunnel junction device based on CrO@sub 2@, and thus opens up new opportunities in magneto-electronics.

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[1] **Falicov Student Award Finalist**

5:00pm **MI-MoA10 Effect of Composition and Microstructure on Temperature Coefficient of Resistance of Polycrystalline La1-xCaxMnO3 Thin Films***, **C.-H. Lai**, C.-F. Hsu,* National Tsing Hua University, Taiwan, R. O. C.*; Y.-C. Chin, C.-T. Jiang,* Chung-Shan Institute of Science and Technology, Taiwan

Perovskite La1-xCaxMnO3 has drawn much attention on account of the colossal magnetosistance. Due to the sharp resistivity drop around the insulator-metal transition temperature (Tp), epitaxial La1-xCaxMnO3 thin films have been demonstrated to be a promising candidate for IR detector (bolometric) application. In this work, polycrystalline La1-xCaxMnO3 films were deposited by using rf sputtering on Si/SiO2 substrates, and the dependence of the temperature coefficient of resistance (TCR) on the film composition and the structure was investigated. When the temperature is higher than Curie temperature Tc, the resistivity of our polycrystalline La1-xCaxMnO3 films follow the "small palaron model", that is, the resistivity can be expressed as R=BTexp(Ea/kT). Consequently, increasing the activation energy Ea increases the TCR value. By adjusting the Ar/O2 flux during depositions or changing the atmosphere of post-annealing, oxygen content can be manipulated. Because precise oxygen content is difficult to measure, the lattice constant of the films was used for the indicator of relative oxygen contents. When oxygen content increased, the Ea and TCR decreased accompanied with the increase in Tp. Ea and TCR value also decreased with increasing Ca content. ESCA results showed that the ratio Mn4+/Mn3+ increased with increasing oxygen (or Ca) content. Since the carrier transportation of La1-xCaxMnO3 is mainly by hopping along Mn4+-O-Mn3+, the increase in the ratio Mn4+/Mn3+ may imply that hopping probability increases, resulting in smaller resistance and Ea. The surface roughness can significantly increase the resistance but the TCR value is about the same. The resistance reduced with the grain growth but the TCR value maintained constant. The TCR value can reach 3%/K at room temperature.

Manufacturing Science and Technology
Room 304 - Session MS-MoA

Challenges in Semiconductor Manufacturing for the First Decade of the 21st Century

Moderator: C.R. Brundle, Applied Materials

2:00pm **MS-MoA1 Chips to Power the Peta-bit Network***, **D. Eaglesham**[1],* Lucent **INVITED**

The net continues to grow at a mind-boggling rate. 1999 was the first year that data traffic exceeded voice. Data traffic in North America continues to double every 6 months. This explosive growth is driven an apparently insatiable demand for bandwidth and continuing improvements in the underlying technology. Electronic switches are rapidly moving up the speed scale from Gb/s to 40 Gb/s, while wavelength multiplexing of these signals drives the capacity of a single fibre up from 10Gb/s, with experimental demonstrations in the multi-Terabit/s range. Bandwidth on a single fibre is likely to top out a little short of a Petabit/s within a few years. The basic technology for data manipulation remains the silicon switch. Transistor scaling has been responsible for much of our ability to move huge chunks of data. I will discuss the level of scaling required in the Pb/day era, and the new transistor structures required to overcome the key technical challenges facing CMOS scaling. I will also discuss the new technologies arising to deliver low-cost highly-integrated networking chips, in particular SiGe BiCMOS technologies. Finally, I will describe an assortment of new technologies including MEMS, and integrated waveguides and modulators, that are starting to change the very core of the network.

2:40pm **MS-MoA3 SOI or USJ?: Laminated Electronics for "Post-Roadmap" CMOS***, **M.I. Current**, S.W. Bedell, I.J. Malik, F.J. Henley,* Silicon Genesis **INVITED**

The many challenges that are projected in the ITRS99 study for fabrication of high-performance planar CMOS transistors on bulk Si for gate dimensions smaller than 60-50 nm (expected in year 2006-2008) clearly point to major changes in standard transistor design, materials and fabrication techniques. Various forms of laminated electronic substrates, beginning with Silicon-on-Insulator (SOI), provide a means to relax some of the process and materials constraints on bulk Si devices. SOI substrates also provide new design options, such as dual-gated channels and high-mobility buried channels. New technologies are now available to bond and cleave electronic materials layers with atomic layer control and surface roughness approaching 1 Å (RMS) without the need for CMP or other damage removal and polishing processes. The design and fabrication of complex laminated electronics "master slice" substrates, which can provide for integrated fabrication of opto-electronic circuits, will be illustrated with examples for such components as dual-gate CMOS, compliant substrates for III-V film growth and optical switching and coupling pathways.

3:20pm **MS-MoA5 The Viability of sub-50nm CMOS Technology***, **G. Timp**, J. Bude, F. Baumann, D. Muller, Y. Kim, M.L. Green, T. Sorsch, D.M. Tennant, R. Kleiman,* Bell Laboratories, Lucent Technologies*; W. Timp,* Massachusetts Institute of Technology*; P. Silverman, B.E. Weir,* Bell Laboratories, Lucent Technologies **INVITED**

The complexity of an integrated circuit (IC), measured by the number of transistors incorporated into the circuit, is constrained by power dissipation. The viability of sub-50nm CMOS technology, which promises to incorporated nearly a billion MOS transistors into one circuit, is contingent upon the drive current performance of the MOSFET as well as the off-state leakage current. We are obliged to pursue improvements in the drive performance to derate the power supply voltage, thereby reducing power dissipation while improving reliability. The drive current of a MOSFET is dictated by both the thickness of the SiO@sub 2@ gate dielectric and by carrier scattering in the channel. Reducing the thickness of the gate oxide increases the drive current by increasing the carrier density in the channel through an increase in the gate capacitance. However, the gate leakage current due to direct, quantum mechanical tunneling through the oxide renders SiO@sub 2@ thickness' less than 1.3nm impractical because the off-state leakage current becomes intoleralbe.@footnote 1@ Consequently, the drive performance for t@sub ox@>1.3nm is limited by ballistic transport in the channel. We have shown that ballistic transport (with transmittance T>0.80) can be achieved at room temperature in a silicon MOSFET operating with transverse electric fields at the inversion layer in the semiconductor >1MV/cm, provided that the deleterious effect of interface roughness scattering is mitigated by optimizing the transverse field and minimizing the channel length and interface roughness. This optimum illustrates the futility of alternative, high @kappa@ gate dielectrics that give rise to a channel mobility less than that found at the equivalent SiO@sub 2@ thickness or operate at higher transverse fields, and indicates that a more sophisticated design of the source, drain and channel doping profiles will be required to satisfy the drive specifications. @FootnoteText@ @footnote 1@ D. Muller et al., Nature, 399 (1999) 758.

4:00pm **MS-MoA7 Technology for Wired and Wireless Networks***, **S. Subbanna**, B. Meyerson,* IBM Microelectronics **INVITED**

In the first decade of this century, we can expect to see extraordinary growth in the availability of information bandwidth. Telecommunications providers and/or service providers will be expanding their capacity to provide increasing numbers and types of services at an ever cheaper rate. This will drive demand for high-speed wired and wireless ICs, and for the seamless connection of both. This talk will focus on the silicon-based process technology, packaging, and design infrastructure requirements for rapid development and supply of cost-effective solutions. In particular the manufacturing advantages of using a silicon (CMOS) base for this technology will be expounded. One technology that unites the cost-effective CMOS base with a high-performance RF NPN bipolar transistor is Silicon-germanium (SiGe) BICMOS. SiGe BICMOS has been used to combine many different RF and digital functions on a single chip. The drive for RF system-on-a-chip is great due to requirements of power, space, and weight reduction for cellular phones. We will discuss design of the SiGe BICMOS technology for manufacturability, as well as issues associated with bringing our 0.5, 0.25, and 0.18um technologies to production. The issues associated with use of CMOS technologies for RF applications will also be discussed, as well as tooling implications and requirements (which are slightly different than CMOS). The issues associated with simulation of (semiconductor) processes and device performance for SiGe BICMOS will also be discussed. We will also discuss challenges for improvement of yield and manufacturability of these technologies. We will also review the limits on silicon technology performance in the light of these new developments.

4:40pm **MS-MoA9 Process Integration Challenges in a Copper/Low-K World***, **R.A. Powell**,* Novellus Systems **INVITED**

It is generally agreed that the wiring of GigaHertz-class ICs will be a multilevel interconnect stack of Cu lines electrically insulated from each other by low-k interlevel dielectrics and assembled using a Damascene process flow. Significant progress has already been made on unit processes

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[1] **Featured Speaker - Science and Technology in the 21st Century**

needed for 0.10-0.13 µm technology, including deposition of conformal barrier/seed layers by ionized PVD or CVD, bottom-up filling of vias and trenches using additive-enhanced Cu electroplating, and deposition and patterning of CVD and spin-on dielectrics having dielectric constant in the range 2 < k < 3. On the other hand, integrating these unit processes together without losing the intrinsic material benefits of Cu and low-k dielectrics is a major challenge and requires a balance between performance, reliability and cost. The present talk illustrates how the distinctive physical and chemical properties of Cu and low-k dielectrics are influencing integration schemes as well as presenting new opportunities for process equipment and metrology suppliers. Examples will include issues of wafer-scale and micro-scale Cu contamination; the impact of water vapor exposure and degassing on low-k dielectric performance and film adhesion; and the development of reactive pre-cleaning and annealing methods to deal with the non-passivating nature of the Cu surface.

Nanotubes - Science and Applications
Room 309 - Session NM+NS-MoA

Carbon Nanotubes: Nanoelectronics and Field Emission

Moderator: S. Sinnott, University of Kentucky

2:20pm **NM+NS-MoA2 Analysis of Long-Channel Nanotube Field-Effect-Transistors (NT FETs)**, ***T. Yamada,*** NASA Ames Research Center

Recent experiment on carbon NT p-channel FETs with a long channel (3 µm)@footnote 1@ is analyzed theoretically. They observed saturation of drain current (I@sub d@) as a function of drain voltage (V@sub d@), which plays a crucial role in digital applications. Two possible mechanisms can make the carrier acceleration by V@sub d@ ineffective and bring about the I@sub d@ saturation: (1) Coulomb repulsion from other carriers forming a self-consistent spatial distribution, leading to channel pinch-off; (2) phonon scattering due to a large field created by V@sub d@, leading to carrier velocity saturation. Since the former causes the saturated current I@sub dsat@ to depend quadratically on gate voltage (V@sub g@) and the latter linearly, two mechanisms are distinguishable. Noticing the quadratic dependence in their measurement, we argue that the Coulomb-induced pinch-off formation was the mechanism in these long-channel NT FETs. The maximum field was about 10 kV/cm and the velocity saturation for holes still did not occur. This field is comparable to that of electrons in silicon. |I@sub d@|-V@sub g@ characteristics did not show a sharp rise at the onset of strong inversion, during the transition from accumulation to inversion, as V@sub g@ was increased. This is significantly different from the familiar behavior of metal-oxide-semiconductor FETs. In NT FETs, I@sub d@ was practically zero for a wide range V@sub g@ = 3 to 40 V beyond accumulation. We argue that a high Schottky barrier for electrons existed at the source/drain metal-semiconductor contact and the electron flow was blocked in the inverted case although the hole flow was not in the accumulated case. Making Ohmic contact to both p- and n-NTs is mandatory for complementary circuitry, and will have to be explored for future electronics. @FootnoteText@ @footnote 1@C. Zhou, J. Kong, and H. Dai, Appl. Phys. Lett. 76, 1597 (2000).

2:40pm **NM+NS-MoA3 Electrical Transport in Carbon Nanotubes**, ***Ph. Avouris,*** *P.G. Collins, R. Martel, H.R. Shea,* IBM T.J. Watson Research Center; *H. Stahl, J. Appenzeller,* Physikalisches Institut, Germany **INVITED**

We will discuss studies of the electronic structure and electrical transport properties of individual and ropes of single-wall (SW) and multi-wall (MW) carbon nanotubes (CNTs). Both metallic and semiconducting NTs have been investigated. In the case of metallic NTs we will present results on the observation and interpretation of negative magneto-resistance, weak localization, strong localization, anti-localization, and Coulomb blockade phenomena. In the case of semiconducting NTs, we have observed band-bending, field switching, carrier depletion and inversion phenomena. Some evidence for non-local transport at elevated temperatures in MWNTs will be discussed. In the case of SWNTs ropes we have been able to obtain results on the efficiency of inter-tube electrical transport. Finally, the operation and characteristics of model NT-based devices such as field-effect transistors, single-electron transistors and low-pass filters will be discussed.

3:20pm **NM+NS-MoA5 First Principles Study of Electronic Properties of Molecule Functionalized Carbon Nanotube**, ***J. Zhao,*** *A. Buldum, J.P. Lu,* University of North Carolina at Chapel Hill; *J. Han,* NASA Ames Research Center

We studied the functionalized carbon nanotubes by using first principles methods based on density functional theory (DFT). The adsorption energy and structures are studied for various molecules including: O@sub 2@, N@sub 2@, H@sub 2@O, NO@sub 2@, CO@sub 2@, NH@sub 3@, He. The electronic structures calculations show that SWNT can be either charge donor or acceptor depending on the molecule. Thus the conductive properties of SWNTs can be dramatically changed by exposing to gases.

3:40pm **NM+NS-MoA6 Effect of Commensurate Contact on the Resistance Across the CNT/HOPG Interface**, ***S. Paulson,*** *M.R. Falvo, A. Seeger, R.M. Taylor II, S. Washburn, R. Superfine,* The University of North Carolina

We report measurements of the effect of atomic interlocking on the mechanical behavior and electrical conduction between bodies. We have manipulated carbon nanotubes on an HOPG substrate with a conducting AFM tip as an electrical probe. Along with our lateral force evidence of commensurate contact, we present the first data measuring the change in contact resistance between two atomically smooth surfaces as they go between the commensurate and incommensurate states. The conducting AFM tip contacts the CNT from the top and current is collected in the HOPG substrate, therefor our measurement of resistance is across the CNT diameter as opposed to its length. We find very low resistance for this circumferential current as compared to longitudinal currents that have been reported. Our results will be interpreted in light of models of coupling between the tip and the various electrical modes in the CNT. This work was supported by the National Science Foundation (HPCC, ECS), the Office of Naval Research (MURI), and National Institutes of Health (NCRR).

4:00pm **NM+NS-MoA7 Ultra-Low Bias Operation of Field Emitter using Single Wall Carbon Nanotube Directly Grown onto Silicon Tip by Thermal CVD**, ***K. Matsumoto,*** Electrotechnical Laboratory, Japan; *S. Kinoshita,* Meiji University, Japan; *Y. Gotoh,* Tsukuba University, Japan; *T. Uchiyama,* Advanced Technology Institute, Japan; *S. Manalis,* Massachusetts Institute of Technology; *C. Quate,* Stanford University

The new carbon nanotube field emitter with single wall carbon nanotubes of a diameter of 1~2nm which were grown directly by thermal CVD onto the Si tips and protruded from them@footnote 1@ was developed. Owing to the 10 to 20 times smaller diameter of nanotube than the conventional Si tip, the new carbon nanotube field emitter showed the ultra-low threshold bias of 10V for the field emission of electron which is more than 10~50 times smaller value than the conventional Si emitter. The n-type silicon was etched by SF@sub 6@gas to form the 10900 silicon tips . After the chemical catalyst was spin coated, the sample was set in the furnace with hydro-carbonate gas flow at high temperature. The single wall carbon nanotube then started to grow and followed up the wall of the silicon tip to the top and protruded from the silicon tip. Three kinds of spacers of 6µm, 10µm, 21µm were prepared to change the distance between the anode and the carbon nanotube emitter. When the spacer is 21µm, the electrons began to emit at the applied bias of ~25V. The narrower the spacer, the threshold bias becomes smaller. When the spacer is 6µm, the electron starts to emit at the applied bias of as small as 10V. In the Fowler-Nordheim plot, the current follows the linear lines in 4~5 orders of magnitudes even at the different spacer thickness, which means the electrons are really field emitted from the carbon nanotube through the Fowler-Nordheim tunneling. This single wall carbon nanotube field emitter could be applicable to any kind of low power consumption flat panel displays in future. @FootnoteText@ @footnote 1@ J. Kong, C. Zhou, A. Morpurgo, H. T. Soh, C. F. Quate, C. Marcus, H. Dai, Applied Physics A69, p. 305, (1999).

4:20pm **NM+NS-MoA8 Field Emission Properties of Vertically Aligned Carbon Nanotubes Dependent Upon Gas Exposures and Growth Conditions**, ***S.C Lim,*** *D.J. Bae, K.H. An, Y.C. Choi, H.J. Jeong, Y.H. Lee,* Jeonbuk National University, Korea

Vertically aligned carbon nanotubes have been grown with different growth conditions by microwave plasma chemical vapor deposition and thermal chemical vapor deposition. The field emission properties of such grown carbon nanotubes are studied. Carbon nanotubes under high bias voltage are exposed to hydrogen, nitrogen, and oxygen. After each exposure, changes on turn-on volatage and slpoe of Fowler-Nordheim plots are observed. The saturation region of emission current at high bias voltage has been shifted. Degradation of field emission current from hydrogen and oxygen exposures has been observed. The ratio of change of emission current shows that oxygen exposure degrades the emission current more severely.

4:40pm **NM+NS-MoA9 Study on Field Emission Mechanism of Carbon Nanotube using High-resolution Electron Microscopy***, **T. Kuzumaki**, H. Ichinose, Y. Horiike,* The University of Tokyo, Japan

In investigation of the relation between the tip structures and the field electron emission characteristics of the nanotube, we have found that the nanotube tip is plastically deformed during cold emission. Our studies with a high-resolution transmission electron microscope reveal that the deformation occurred at the local domain containing an isolated pentagonal carbon ring in the polyhedral cap and a convexity is formed along the electric field direction. Semi-empirical molecular orbital calculations show that the pentagon and heptagon pair is introduced into the hexagonal network with a pentagonal carbon ring by heterogeneous nucleation mechanism, and the resulting convexity structure is formed at the tip. The electron emission characteristics of the closed nanotube show that the threshold voltage was high for the first run and the current increased quickly. After the second run the emission started at rather lower voltage and increased gradually. Fowler - Nordheim (F-N) plots show that the first run does not show a straight line. There is no marked change to gradient the second run. The decreasing of the threshold voltage after the second run is possibly due to the structural change of the nanotube tip. The opened nanotubes also show the notable structural change at the tip. The deformed structure can be explained by introducing sp@super 3@ - like line defects in the hexagonal carbon network. In the opened nanotube, the gradient of the F-N plots is decreasing corresponding to change of structure. The formation of the emission site contributes greatly to the stable and highly efficient electron emission from the nanotubes.

5:00pm **NM+NS-MoA10 A Carbon Nano-Tube Based Electron Gun for Electron Microscopy***, O. Zik,* El-Mul Technologies Ltd., Israel*; **J.G. Leopold,*** Dept. of Appl Phys., Rafael Labs, Israel*; D. Rosenblatt,* Rosenblatt Associates

A novel electron gun geometry is proposed with a carbon nano-tube (CNT) grown in a conducting microfabricated crater separated from a gate by an insulating layer. Electron microscopy preferably utilizes point sources. Field enhancement is responsible for the increased emitted current. The field decreases after a very short range to the free space field of the device and the beam diverges. Because the point source and the electron optics are in practice far from ideal, large angular emission density is required with apertures cropping the diverging beam. Thus, a very small portion of the emitted current is useful. Best performance for point sources is gained when the emitter is a rounded, long and very sharp whisker - a 'point on plane' geometry. Such geometry can be realized with CNT's which have exceptional electron emission properties with very low energy spread. However, due to beam divergence, bare CNT's 'on a plane' are inadequate for Scanning Electron Microscopy (SEM) and to miniature SEM's, termed 'microcolumns', in particular. The crater geometry decreases field enhancement on the tip by an order of magnitude so that increased voltage is needed. Due to the excellent field emission of CNT's this voltage is acceptably low so as to obtain about 500nA while not exceeding the breakdown limit of the insulating layer. Our computer simulations support these results. For such geometry the CNT is immersed in a gun which in itself comprises a lens aligning the beam. Almost all the emitted current can be used in a micro-column. In addition to the low energy spread inherent to CNT's, this electron gun has very high brightness which is an advantage for SEM and lithography applications.

Processing at the Nanoscale/NANO 6
Room 302 - Session NS+NANO6-MoA

Manipulation of Atoms and Molecules

Moderator: J.W. Lyding, University of Illinois, Urbana

2:00pm **NS+NANO6-MoA1 Atomic/Molecular Manipulation with the Low Temperature STM***, **G. Meyer,*** Paul Drude Institut für Festkörperelektronik, Germany **INVITED**

The scanning tunneling microscope (STM) opened up new fascinating possibilities for the development of atomic scale technologies. The force between the STM-tip and a single adsorbate can be used to laterally position atoms/molecules with atomic precision (lateral manipulation), which allows the buildup of small nanostructures in an atom by atom way. By exploiting electric field and inelastic tunneling effects individual molecules can be desorbed, transferred to the STM-tip (vertical manipulation), dissociated or even synthesized. For future applications the basic physical mechanisms controlling these techniques have to be investigated first. As model systems we have studied the lateral/vertical manipulation of single metal adatoms (Cu), small molecules (CO, C@sub6@H@sub 4@I@sub 2@), and large molecules (CuTBPP) adsorbed on metal surfaces (Cu(111), Cu(100), Cu(211)) at low temperatures. Adsorbates can be moved laterally by applying attractive or repulsive forces. This results in a simple pulling or pushing behavior, which can be directly observed in the STM tip height or current signal. In the case of large molecules, which have additional internal degrees of freedom, a more complicated movement behavior is observed. Apart from single adsorbates, also complete chains of molecules can be laterally manipulated and information on the correlated motion of the molecules can be extracted. Finally several examples for the application of the manipulation techniques in the area of surface science will be given. These include: determination of adsorbate binding sites, buildup of small domains of ordered adsorbate phases, atomic scale structuring of the underlying substrate, measurement of weak substrate mediated long range adsorbate interactions, dissociation/synthesis of molecules, manipulation on thin insulating films.

2:40pm **NS+NANO6-MoA3 Fundamental Approaches to Silicon-based Molecular Nanotechnology using the Scanning Tunneling Microscope***, **M.C. Hersam**, N.P. Guisinger, L. Liu, J.W. Lyding,* University of Illinois

The importance of molecular nanotechnology has recently been underscored by increased media, public, and government awareness of the subject. This paper outlines an approach for fabricating and characterizing single molecule units on the technologically significant Si(100) surface with the ultra-high vacuum scanning tunneling microscope (UHV-STM). Using feedback controlled lithography (FCL), individual H atoms can be removed from the Si(100)-2x1:H surface. The remaining dangling bond patterns serve as atomically precise templates upon which other materials can spontaneously self-assemble. By utilizing this selective chemistry in situ, several organic molecules (e.g., norbornadiene (NBE), copper phthalocyanine (CuPc), C@sub 60@, etc.) have been isolated. The mechanical, chemical, and electronic properties of these individual adsorbed species can then be immediately detected with the STM. For CuPc, the spatial extent of charge transfer from the substrate to the adsorbate is measured as a function of binding orientation. When the CuPc is reduced with ammonia, single molecule rotation is observed. STM spectroscopic measurements on C@sub 60@ reveal intra-molecular variations in the electronic density of states. A fundamental understanding of such phenomena will enable the design of nanoscale devices. For electronic applications, the application of lateral electrical fields to individual molecules is crucial. A fully compatible electrical contacting scheme based on p-n junctions will be presented. Efficient STM potentiometric location of these p-n junctions suggests their additional use as alignment markers. Finally, the robustness of this technique will be outlined. Even following exposure to ambient conditions, the in situ H-passivated Si(100) surface remains atomically pristine. The ability to combine nanolithography with wet chemical processing opens up new opportunities for nanoscale chemical and biological applications.

3:00pm **NS+NANO6-MoA4 STM Atom Manipulation***, **D.M. Eigler**,* IBM, Almaden **INVITED**

PLEASE SEND US AN ABSTRACT. Thank you.

3:40pm **NS+NANO6-MoA6 Scanning Tunneling Spectroscopy via Adsorbate Resonances: Kondo vs. Non-magnetic Systems***, **M. Plihal**, J.W. Gadzuk,* National Institute of Standards and Technology

Resonance tunneling STM studies of transition metal atoms adsorbed on noble metal surfaces, some combinations forming Kondo systems defined by the presence of a localised magnetic moment on the adsorbate and a spatially extended spin compensation cloud within the substrate, have recently been reported. The intriguing additional influence of artificially-synthesized boundaries such as other atoms, quantum wires, and quantum corrals on the surface has also received much attention. Typically the spectroscopic results are given as spatially-dependent differential conductance versus voltage spectra, usually observed to be close in form to an asymmetric Fano lineshape. This form is characteristic of the interfering "decay" of an initially excited localized state (here an electron or hole state within the STM tip) into a continuum which has been perturbed by a discrete localized state (here the substrate conduction band states coupled to the adsorbate valence electron states). We sketch a detailed theory of the spectral properties of the tunneling for such systems valid for arbitrary intra-adsorbate electron-electron interactions, taking into account nonequilibrium effects when tunneling into the resonance is strong in comparison with direct tip-to-surface tunneling. We present the temperature and tip-position dependence for tunneling through both a Kondo resonance and that of a non-interacting, hence non-magnetic adsorbate. Most of the predicted tunneling characteristics are common to both types of resonances. Issues associated with the spatial dependences, including impurity scattering and mirages within corrals are treated in a natural way using our model.

4:00pm **NS+NANO6-MoA7 Manipulation and Inelastic Tunneling Spectroscopy Measurement of CO on Pd(110) using Low-temperature STM***, **T. Komeda**, Y.S. Kim, M. Kawai,* Riken, Japan

The ability of the scanning tunneling microcopy (STM) to manipulate a single molecule adsorbed on metal surfaces and induce local chemical reaction makes it an idealistic tool to investigate fundamentals of chemical reactions and the catalytic phenomena. In addition, the recent success of inelastic tunneling spectroscopy (IETS) to obtain chemical information by measuring its vibration state makes it more attractive. In this paper, we show the results of the manipulation and the IETS measurement by STM on carbon monoxide (CO) adsorbed on Pd(110) surface at the temperature of 4.8 K. Intriguing 1D chains of CO molecules along Pd(110) row ([-110] direction) was observed at very low-coverage region which grew to islands with local ordered structure of c(2x2). No movement of the molecule was observed during the STM measurement (tunneling current of 1nA with bias of 100 mV) for the temperature range upto 40 K. The manipulation on isolated CO molecules were done with the following method. The tip was positioned to give 0.1 nA tunneling current with 10mA substrate bias, then feedback loop was turned off. The bias between the tip and the sample was varied between -350 mV and +350 mV with the frequency of 3Hz which gives the maximum current less than 5 nA which is quite moderate for metal observation. However, this method caused the CO molecule hopped single site along [-110] direction. The driving force for the CO movement can be understood by the interaction between the electric field formed by the tip-and-sample and the dipole-moment of CO, which is considered to be very controllable method without touching between the tip and the sample. Also inelastic tunneling spectroscopy (IETS) has been carried out on an isolated CO molecule and on the CO chains. The I-V curve showed characteristic features around 250 mV.

4:20pm **NS+NANO6-MoA8 Benzene and Its Derivatives on Transition Metal (111) Surfaces***, **Y.-J. Song**, J.-Y. Park, U.D. Ham, H.J. Kim, Y. Kuk,* Seoul National University, Korea

Benzene and its derivatives such as bromobenzene, iodobenzene, and xylene, adsorbed on transition metal surfaces (Cu and Pd) have been investigated with an ultrahigh vacuum low temperature scanning tunneling microscope (STM). At room temperature, these molecules are highly mobile so that it is difficult to study low coverage behaviors. On the other hand, they form close-packed ordered structure with three different domains at saturation coverage, as observed with STM. At low temperature, the mobility of molecules is reduced that single molecules can be studied. With high-resolution imaging capability of our STM, internal structures of molecules are revealed. Therefore, different isomers can be distinguished. Furthermore, manipulation of these molecules is performed with the STM tip. Possible mechanisms of different manipulation modes will also be discussed. The possibility of STM-induced molecular reaction will also be presented.

4:40pm **NS+NANO6-MoA9 Artificial Surface Structure on H/Si(100)4x3-In Surface Using STM Tip***, **O. Kubo**, T. Harada, T. Kobayashi, N. Yamaoka, M. Katayama, K. Oura,* Osaka University, Japan

Scanning tunneling microscopy (STM) recently has considerable attention as an apparatus not only for observation of surface structures but also for manipulation of surface atoms. Since Lyding et al.@footnote 1@ reported about hydrogen (H) extraction from Si(100)2x1-H (monohydride) surface using STM tip, H extraction has been investigated both experimentally and theoretically. When superstructures on Si surface induced by metal (Ag, In, etc.) adsorption are exposed to atomic H, peculiar H terminated surface phases are induced. For instance, Si(100)4x3-In surface phase is produced by the deposition of 0.5ML In onto Si(100)2x1 surface at 400°C. When this surface is exposed to atomic H at 300°C, In atoms form clusters, and the reconstructed Si layer which have been formed under In layer is frozen by H termination of Si dangling bonds.@footnote 2@ This H terminated Si layer has monohydride dimer rows whose interval is 4a (a = 3.84 Å), and among the dimer rows, it has dihydride Si atoms (what we call Si(100)4x1-H). In this study, we have performed H extraction from the Si(100)4x1-H surface using STM tip. The H extraction could be performed by applying about 5 V of sample voltage and about 0.2 nA of tunneling current, which were almost the same condition for the H extraction from Si(100)2x1-H. After H extraction, the 4a periodicity of dimer rows was preserved and the H extracted area was observed higher than a surrounding H terminated surface as well as the extracted area on Si(100)2x1-H surface. This result means that peculiar Si surface structure can be formed artificially. The dimer rows consisted of buckled dimers in spite of room temperature observation contrary to the case on Si(100)2x1-H surface. It is most likely that these dimers were induced by surface stress as same as seen on step edges. @FootnoteText@ @footnote 1@ J.W. Lyding et al., J. Vac. Sci. Technol. B 12 (1994) 3735 @footnote 2@ J.T. Ryu et al., J. Vac. Sci. Technol. B 17 (1999) 983.

5:00pm **NS+NANO6-MoA10 Adsorption and Manipulation of Endohedral Fullerenes on Silicon Surfaces***, M.J. Butcher, **P.H. Beton**,* University of Nottingham, UK*; P. Kuran, L. Dunsch,* IFW Dresden, Germany

The adsorption and manipulation of an endohedral fullerene, LaC82 has been investigated using a scanning tunnelling microscope (STM) operating at room temperature in ultra-high vacuum. These molecules are adsorbed on top of both rows and troughs on the Si(100)-2x1 surface, and like C60 may be manipulated in a repulsive mode using the STM tip. However for LaC82 a much stronger interaction between adsorbate and tip is required to promote manipulation resulting in a lower voltage threshold for this process. Adsorption of this species on a less reactive substrate (for example, Ag/Si(111)) results in the formation of close packed hexagonal islands oriented, primarily, parallel to the principal axes of the Si surface. This result confirms an expected commensurability of the intermolecular spacing, d, and the surface lattice constant, namely d~3a, indicating that it should be possible to form close packed rows of LaC82 along the troughs of Si(100)-2x1. The formation of pairs and other simple close packed assemblies of molecules has been demonstrated. A comparison of the response to manipulation of a range of fullerenes and heterofullerenes will also be presented and discussed in terms of the effects of size and chemistry of the adsorbed molecules.

Plasma Science and Technology
Room 310 - Session PS1-MoA
Emerging Plasma Applications

Moderator: V.A. Shamamian, Naval Research Laboratory

2:00pm **PS1-MoA1 A Surface-Micromachined Miniature Inductively Coupled Plasma Generator***, **J.A. Hopwood**, O. Minayeva, Y. Yin,* Northeastern University **INVITED**

The design, fabrication, and characterization of a surface micromachined plasma generator are described. Although there are many applications for miniature plasma sources, this device is intended for electronic excitation of gas samples such that the presence of impurities and toxins may be detected using a micromachined optical emission spectrometer. The plasma is sustained without electrodes by inductively coupling a 450 MHz current into a region of low-pressure gas. The inductively coupled plasma source is surface micromachined on a glass substrate by electroplating a planar spiral inductor (5 mm in diameter) and two interdigitated capacitors. A plasma can be sustained in argon and air between 0.1 and 10 torr (13.3 Pa - 1333 Pa) and rf powers between 0.3 and 3 W. The argon ion density increases from 10@super 10@ to 10@super 11@ cm@super -3@ over this range of powers. The electron temperature decreases from 4 eV to 2 eV as the pressure increases from 0.1 to 1 torr. Network analysis of the plasma generator circuit shows that over 99% of the applied RF power can be absorbed by the device. Of this, @<=@50% is absorbed by the plasma and the remainder of the power is dissipated as ohmic heating. Scaling laws associated with the miniaturization of inductively coupled plasma sources will be discussed including the dependence of electron temperature on scaled chamber dimensions, the preferred frequency of operation, and rf power coupling efficiency.

2:40pm **PS1-MoA3 Physics of Hollow Cathode Magnetron (HCM) Plasma Source***, **K.F. Lai**,* Novellus Systems, Inc.

The hollow cathode magnetron (HCM) is a new type of high-density plasma device developed for ionized physical vapor deposition (I-PVD). A novel magnetic geometry provides the confining magnetic field to sustain a magnetron discharge within a cup-shaped hollow cathode and the means of ion extraction from the source to the substrate. The use of a "cusp mirror" to reflect most of the escaping electrons back into the hollow cathode cavity has allowed the HCM to achieve extremely high plasma density (10@super 12@ - 10@super 13@ cm@super -3@). The HCM source is highly scaleable and has been successfully implemented in sources ranging from 19 to over 380 mm in diameter. Although the HCM has proven to be a very successful I-PVD source, there is a lack of understanding about its detail working mechanisms. Recent progress in three dimensional electrical probe measurements together with plasma modeling have revealed a different physics picture from our previous belief. Strong radial electric field on the order of 400 V/m was measured inside the hollow cathode. In conjunction with the confining magnetic field, a large ExB drift current is established because of the magnetron effect. As a result of this current and the incomplete shielding of the cathode voltage, the measured plasma density profile inside the cathode is hollow and funnel-shaped. The density profile becomes Gaussian as the plasma emerges through the magnetic null. Unlike other downstream plasma sources where the plasma density near the source is much higher than that downstream, no significant difference in plasma density is observed for the HCM. With the exception of the plasma edge where the presence of an energetic electron tail was evident, the electron energy distribution (EEDF) was approximately Maxwellian. Despite more than two orders of magnitude variation in plasma density, the electron temperature profile is relative flat throughout the entire plasma.

3:00pm **PS1-MoA4 Ion-Ion Plasma Formation and Negative Ion Extraction***,*

S.K. Kanakasabapathy[1], *M.H. Khater, L.J. Overzet,* University of Texas, Dallas

Ion-ion plasmas are relatively electron-free, positive and negative ion only plasmas formed in the afterglow of Pulsed-power high electron affinity gas@footnote 1@ (Eg: Cl@sub 2@) discharges. They hold the potential to provide ambipolar fluxes of positive and negative ions that could reduce differential charging of high anisotropy structures which cause@footnote 2@ etch non-idealities. Time-resolved Langmuir probe and Microwave Interferometry measurements in a pulsed ICP discharge show that electrons are quickly lost (~ 10's of µmsecs) to dissociative attachment after turning power off. Time-resolved mass spectrometry has correlated the vanishing of electrons and consequently the confining plasma potential to the incipience of a negative ion (Cl@super -@) surface flux. Parametric characterization of Pulsed Cl@sub 2@ discharges has indicated that low pressures (1 mTorr), high powers (300 W peak), mid duty ratios (50%) and low pulse frequency (500 Hz) maximize this negative ion flux. Langmuir probe ion density decay rate measurements have shown ion-ion recombination to be the dominant loss process. We observe reproducible alternating irradiations of positive (Cl@sub 2@@super +@) and negative (Cl@super -@) ions corresponding to the negative and positive half-cycles respectively when a low frequency (20 kHz) bias applied to the mass spectrometer pinhole. This bias is applied as a phase-locked burst that is synchronized with the formation of ion-ion plasmas. Parametric characterization of this novel extraction technique reveals a bi-modal frequency response of the Cl@super -@ surface flux. This presentation is based upon work supported by the NSF under Grant No. CTS-9713262. @FootnoteText@ @footnote 1@D. Smith, A.G. Dean and N.G. Adams, J. Appl. Phys. 7, 1944-1962(1974) @footnote 2@G.S. Hwang and K.P. Giapis, J. Appl. Phys. 81(8) 3433-3439(1997).

3:20pm **PS1-MoA5 Large Area Plasma Processing System Based on Electron Beam Ionization***,*

D. Leonhardt*, S.G. Walton, D.D. Blackwell, W.E. Amatucci, D.P. Murphy, R.F. Fernsler, R.A. Meger,* Naval Research Laboratory

Electron beam ionization is both efficient at producing plasma and scalable to large area (square meters). The beam ionization process is also fairly independent gas composition, capable of producing low temperature plasma electrons in high densities. A 'Large Area Plasma Processing System' has been developed based on the beam ionization process, with the goal of modifying the surface properties of materials over large areas. The system consists of a planar plasma distribution generated by a magnetically collimated sheet of 2-5kV, ~ 10 mA/cm@super 2@ electrons injected into a neutral gas background (oxygen, nitrogen, argon, neon). Typical operating pressures range from 20-200 mtorr with beam-collimating magnetic fields strengths of 100-300 Gauss. Thus far, electron beams have been produced using pulsed (10-4000 ms pulse length, >50% duty cycle) and dc hollow cathode discharges in dielectric as well as conducting chambers. Temporally resolved plasma characteristics deduced from Langmuir probes, optical emission spectroscopy and microwave transmission measurements will be presented. Over large areas (2 cm x 60 cm x 60 cm), results show low electron temperature (T@sub e@ ~ 0.6 and 1.5 eV in molecular and noble gases, respectively) in a bulk diffusion-dominated plasma with densities ranging from 10@super 9@ to 10@super 12@ cm@super -3@. Temporally resolved plasma-to-surface fluxes (via mass spectrometry) and their energy distributions will be presented to give further insight into LAPPS for material processing applications. If time permits, additional photoresist ashing tests demonstrating anisotropic pattern transfer will be discussed, along with design improvements in the electron beam source. Additional details of in situ diagnostics in LAPPS will also be presented by co-authors.@footnote 1@ @FootnoteText@ S.G. Walton, D.D. Blackwell - NRL/NRC Postdoctoral Research Associates @footnote 1@ See other presentations by co-authors at this conference.

3:40pm **PS1-MoA6 New Development of Plasma Technology for Biomaterial Engineering***,* **INVITED**

1. Introduction There has recently been increasing interest in the applications of plasma processing in a variety of industrial fields. One of applications of organic plasma processing now in practical use is plasma treatment. One of the advantages of plasma treatment is the fact that it is surface limited (500-1000Å) so that only the surface properties can be changed without affecting the bulk properties. In view of the fact that surface reactions of plasma treatment are initiated by plasma-induced surface radicals, study of the resulting radicals is of utmost importance for understanding of the nature of plasma treatment. Thus, we have undertaken plasma-irradiation of a wide variety of polymers, synthetic and natural, and the radicals formed were studied by electron spin resonance(ESR) coupled with the aid of systematic computer simulations. On the basis of the findings from a series of such studies, we were able to develop several novel biomedical application works in the field of biomaterial engineering. In this contribution, our novel application works in drug engineering on plasma-irradiated organic polymers will be presented, which include (1) preparations of multilayered tablet applicable for drug delivery system(DDS)of sustained- and delayed-release, (2) fabrication of functionalized composite powders derived from plasma-irradiation onto powdered polymers followed by mechanical applications in the presence of powdered drugs under anaerobic conditions,(3) preparation of biocompatible biomedical polymer surface useful for cathetal, as well as overviews of ESR studies on plasma-induced radicals of a variety of organic polymers.

4:20pm **PS1-MoA8 Detection of Perfluorinated Compounds by Microplasma Optical Emission Spectroscopy***,*

D.D. Hsu*, D.B. Graves,* University of California, Berkeley

Because of impending restrictions on the emission of perfluorinated compounds (PFCs) by the semiconductor and other industries, methods for monitoring PFC concentrations in exhaust streams will be necessary. Current methods, including Fourier transform infrared (FTIR) spectrometry and mass spectrometry, are relatively expensive and complicated. One option to detect PFCs in exhaust streams at atmospheric pressure is the use of optical emission spectroscopy (OES) from a microhollow cathode discharge (MHCD). These intense glow discharges can be stabilized at elevated pressures and therefore offer the opportunity to exploit OES under a relatively wide range of conditions. This technique presents an inexpensive and simple way to monitor PFC concentrations. The circular geometry of a microhollow cathode produces intense excitation and hence, a strong source for OES. In the results we will present, various concentrations of PFC in a diluent gas were flowed through an MHCD with a hole diameter of 200 µm, and the optical emission was analyzed. A direct current of 8 mA and a voltage of 250 V were supplied to sustain the MHCD. Concentrations as low as 10 ppm C@sub 2@F@sub 6@ in argon at 700 Torr were detected by examining atomic carbon, atomic fluorine, and molecular C@sub 2@ spectra in the visible range. A linear relationship between PFC concentration and integrated emission intensity was found. The results suggest that fluorocarbon concentrations on the order of 1 ppm can be detected with this technique. Details of the experimental setup and the observed spectra of various PFC concentrations in different diluent gases will be discussed. In addition, the results obtained suggest that MHCD OES might be a powerful analytical tool for other species as well.

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

Plasma Science and Technology
Room 311 - Session PS2-MoA

Plasma Etching of Conductors

Moderator: A. Kornblit, Bell Laboratories, Lucent Technologies

2:00pm **PS2-MoA1 Gate Engineering for sub 50 nm CMOS Devices*, J. Foucher,*** CNRS/LTM, France*; G. Cunge,* CEA/LETI, France*; D. Fuard, R.L. Inglebert, L. Vallier, O. Joubert,* CNRS/LTM, France

In less than ten years, we will be approaching the limits of the CMOS technology with typical gate transistor length of less than 30 nm. In the past, gate etch processes have been optimised to provide perfectly straight sidewalls while maintaining the selectivity to the ultra-thin gate oxide (less than 2 nm). Recently, a new approach has been proposed in which the process is tuned to obtain a silicon-based gate whose dimension is smaller at the bottom than at the top of the gate (notched gate). This new approach opens up the possibility of making gates with dimensions smaller than the ultimate resolution of the lithography. In this paper we discuss the mechanisms involved in the fabrication of notched gate. Experiments have been conducted on a very powerful plasma etch system dedicated to advanced studies. It consists in a Decoupled Plasma Source (DPS) from Applied Materials modified to host in situ diagnostics such as UV-visible ellipsometry, mass spectrometry, fast injection Langmuir probe and X-ray photoelectron spectroscopy (XPS). Oxide masked a-si gates are etched using a modified etch recipe allowing a lateral erosion of silicon to be obtained at bottom of the gate. This can be achieved by tuning the thickness and composition of the passivation layer formed on the silicon sidewalls (sidewall passivation layer engineering). The robustness of the sidewall passivation layer is reinforced in the first part of the process while, on the other hand, plasma conditions are tuned in the second part of the process to suppress the passivation layer. In a last step, lateral erosion of the silicon sidewall is possible at the location where no passivation layer has been formed. XPS data of the passivation layer formed at the different process steps will be shown as well as some details on the control of the notch depth. Finally some results showing gate dimension in the 20 nm range will be shown.

2:20pm **PS2-MoA2 Fabrication of 80 nm PN-poly/metal Gate on Ultra-thin 1.5 nm Oxynitride*, K. Kinoshita*,** *S. Saito, Y. Saito, M. Narihiro, M. Ueki, H. Wakabayashi, Y. Ochiai, T. Mogami, Y. Hayashi,* NEC Corporation, Japan

A PN-poly/metal gate is thought to be the promising technology to embedded LSIs beyond 0.13 µm design rule. This paper describes about the 80 nm PN-poly/metal gate fabrication technique on ultra-thin 1.5 nm gate oxynitride. Mix & match resist pattern by a point-beam EB system (JEOL, JBX-9300FS) for sub-0.1 µm pattern, and a usual KrF lithography system for wider pattern were developed over CVD-SiO@sub 2@/W/barrier/PN-poly-Si/gate-oxynitride stack on "8 wafer. The resist mask was transferred to CVD-SiO@sub 2@ hard mask layer, and then the poly/metal stack etching were investigated with a single chamber of an ICP type etcher (AMAT, Silicon Etch Centura DPS). The use of N@sub 2@-rich N@sub 2@/SF@sub 6@/Ar gas system for W etching, and the use of HBr/Cl@sub 2@/O@sub 2@ gas system for TiN etching generated rectangular cross section. Then, the PN-Poly-Si layer was etched by HBr/O@sub 2@ gas system. There existed the important correlation between relative oxygen density change by an optical actinometry and the PN-poly-Si etching. As the O@sub 2@ flow increased, the oxygen density increased, and the local etching to the silicon substrate through the thin gate oxynitride effectively suppressed. However, the excess O@sub 2@ flow brought etching stop on P-poly-Si region. XPS analysis for the etched P-Si wafer showed that the thicker oxide formation on the P-Si wafer etched at the etching stop condition. These results indicated that the P-Si surface oxidation brought both the high etching selectivity and the etching stop. The thinner the gate oxynitride, the narrower the process margins. Finally, good device characteristics were achieved.

2:40pm **PS2-MoA3 Etch Rate Enhancement and Surface Roughening during W/Poly Si Stack Gate Etching Process*, H. Morioka,*** *M. Nakaishi, T. Ishida,* Fujitsu Limited, Japan

W/Poly Si stack structure is one of the most promising candidates for gate electrodes of ULSI in the next generation because of its low sheet resistance and compatibility with self-aligned contact process. But most etching processes of W/Poly Si stack gate have some distinctive problems closely related to W and W etching byproduct, such as non-uniform etch rate enhancement, serious RIE-lag, and profile anomalies. We examined the catalytic effect of W and W etching byproducts on W/Poly Si stack gate etching. Our experiments were performed on a high-density plasma etcher. The chemistry was halogen-base and oxygen was used as an additional gas, which is sometimes utilized for increasing W etching selectivity to poly Si by inhibiting Si etching. An etching sample was poly Si or SiO@sub 2@ wafer on which a W chip was attached in the center. The W chip, which was the only source of W and W etching byproduct, was etched together with the sample wafer in the reaction chamber. The etch rates were measured as a function of distance from the W chip, and the surface roughness was measured by AFM. In this experiment, we found that W and W etching byproducts enhanced the etch rate of poly-Si and SiO@sub 2@, and the enhancement depended on distance from the W chip. The etch rate was maximum near the W chip. Besides, AFM observation revealed the increase of etch pits along grain boundaries on etched poly Si surface, and the increase of roughness of etched SiO@sub 2@ surface when they were etched with the W chip. These facts suggest that W etching byproducts and their fragments decomposed in the plasma are deposited on the sample surface and vary the etching characteristics.

3:00pm **PS2-MoA4 A Drift of Selectivity Depending on Chamber Seasonings in a Poly-Si/Oxide Etching Process using Inductively Coupled Plasma*, K. Miwa,*** Fujitsu VLSI Ltd., Japan*; T. Mukai, M. Nakaishi,* Fujitsu Ltd., Japan

Chamber seasonings after plasma cleanings are useful to stabilize reactor conditions. However, etch-selectivities of poly-Si to oxide with the same recipe were found to drift depending on seasoning methods. After bare-Si wafers were etched with an ICP of HBr/O2 as Si-seasoning, over-etch rates of oxides with the ICP slightly raised and decreased to stop as Si-seasoning time was longer. In cases of blanket-oxide wafers were etched as Oxide-seasoning, over-etch rates of oxides hardly drifted. Over-etch rates of poly-Si were nearly constant after the Si-seasoning or the Oxide-seasoning. Consequently, the etch-selectivity of poly-Si to oxide drifted after the Si-seasoning. Optical emission intensity of SiBr/He in the over-etch plasma increased with increase of Si-seasoning time. Over-etch rates of oxides also drifted as functions of O2 flow rate and Bias Power to the bottom electrode of the ICP-Etcher. The Deposition formed on the oxides during over-etchings after the Si-seasoning were identified as sub-oxides of Si using X-ray Photoelectron Spectroscopy (XPS). These results suggest that etch-rates of oxides are enhanced and decreased by etch-products such as SiBrx (x=1, 2, 3) in the over-etching plasma derived from the deposition on the reactor wall. The deposition would be formed during the Si-seasoning. When SiBrx coverages of the oxide surface are smaller than saturated coverage, the over-etch rates of oxides would be enhanced due to formation of silicon-oxybromide assisted with incident ions toward the surface. In cases of SiBrx coverages are larger than saturated coverage, excess SiBrx react with Oxygen atoms in the plasma to deposit sub-oxides of Si on the oxide surface. The sub-oxides would inhibit or stop the over-etching of oxides.

3:20pm **PS2-MoA5 Novel Dry Etch Chemistries for Metals*, A. Orland,*** Auburn University*; R. Blumenthal,* Auburn University, usa

Magentic metals are the principle components of the read/write heads and magnetic media of the data storage industry and are even finding their way into semiconductor processing. Although "lift-off" techniques, ion milling and non-specific plasma etches have proven adequate for the fabrication today's devices. These methods are simply not capable of fabricating the structures that will be required for the next generation of devices. Many promising chemistries have failed when involatile products form instead of the desired volatile products. This is likely the case for the etching of Fe and Co with CO/NH@sub 3@, where the formation of low vapor pressure dimeric species, such as Fe@sub 2@CO@sub 9@ (as opposed to the high vapor pressure monomeric species, FeCO@sub 5@) may be responsible for the low etch rates that have been previously reported in literature. Modification of the CO/NH@sub 3@ chemistry with the addition of methane, acetone, and/or H@sub 2@ to the mixture will be reported. Addition of these species is intended to result in both methyl and acetyl substitutions on the metal, which are known to inhibit the formation of undesirable, non-volatile, dimeric metal complexes. Other results will include the investigation of new chemistries, such as cyclopentadienyl-carbonyl- chemistries, which will explore entirely new classes of possible volatile metal products. In-situ monitoring with supersonic pulse, plasma sampling mass spectrometry will yield information about all chemical species (both monmeric and dimeric) in the plasma environment, hence, it will provide a basis for understanding the chemical mechanisms of both successful and unsuccessful new etch chemistries.

3:40pm **PS2-MoA6 Experimental and Modeling Results for Process Scaling from 200 mm to 300 mm Wafers***, **S.C. Siu**, D. Cooperberg, V. Vahedi, R. Patrick,* Lam Research Corporation

As the wafer fabrication industry begins to move from 200 mm to 300 mm wafers, the need arises to transfer existing processes both to larger wafers and to larger process chambers. Transferring a 200 mm baseline process to a 300 mm chamber is not trivial, but it is critical for quick ramp up from development to production. For next generation process chambers that can handle both 200 mm and 300 mm wafers, such as those from Lam Research Corporation, process scaling to larger wafers is less complicated because the chamber is fixed, but there are still issues which need to be understood. A successful process transfer will result in enormous savings in time and resources that can be better used to fine tune processes for 300 mm wafers, instead of re-establishing a 300 mm baseline process. Zeroeth order scaling principles previously derived and published by Lieberman and Lichtenberg@footnote 1@ are examined in this paper, and their applicability to practical process scale up are determined. Plasma parameters important in conductor etching, such as ion density, radical concentration, and sheath potential, were measured in a Lam Research 200 mm etch chambers and compared with measurements made in the next generation 300 mm etch chambers. Preliminary results show good agreement between the scaling predictions and plasma measurements. Modeling results show that reactor scaling parameters are application dependent. Scaling parameters for ion dominated etching may differ from those in which etch rate and profile evolution are more dependent on radical concentrations (e.g. resist trim, aluminum etch in chlorine). Additionally, predictions for process scaling may be dependent on the relative importance of radical depletion mechanisms (e.g. wall recombination, reaction, volume loss, pumping effects). @FootnoteText@@footnote 1@M. A. Lieberman and A. J. Lichtenberg, Principles of Plasma Discharges and Materials Processing, John Wiley & Sons, Inc. (New York, 1994), chapter 10.

4:00pm **PS2-MoA7 Improving Al Etch Processing in a High Density Plasma Reactor with a Faraday Shield***, **D.A. Outka**, S.C. Siu, N. Williams,* Lam Research Corp.

As etch geometries become smaller, the uniformity of the reactor environment becomes increasingly important in achieving consistent results within a wafer and from wafer-to-wafer. This study examines the addition of a Faraday shield (FS) to an HDP (high-density plasma) reactor to aid in achieving this goal. The effect of the FS on Al etching is examined with wafer-level, plasma, and electrical diagnostics. The FS is an electrostatic shield inserted between the RF coil and the plasma. With this shield there is approximately a 10% reduction in the Al and oxide etch rates depending upon the RF power. Langmuir probe measurements indicate that this reduction is due mainly to a decrease in the plasma density. Electrical measurements of the impedance of the load with a RF probe were also performed and the results compared with a circuit model. These results also indicate a reduced coupling between the RF coil and the plasma. Based upon these results the impact of adding a FS to a commercial etch tool in terms of wafer performance and productivity is discussed.

4:20pm **PS2-MoA8 Transfer Etch Profile Control for 248 nm Bilayer Thin Film Imaging***, **S. Halle**, R. Wise, J. Brown,* IBM Microelectronics*; O. Genz,* Infineon Technologies Corporation*; A. Thomas, T. Dyer,* IBM Microelectronics*; A.P. Mahorowala, M. Angelopoulos,* IBM T.J. Watson Research Center*; S. Johnston,* Lam Research Corporation

The technique of bilayer thin film imaging and transfer etch is expected to play an important role for extending 248 nm lithographic patterning to 135 nm and below feature sizes. Previous studies have demonstrated the utility of an O@sub 2@/SO@sub 2@ process in a poly TCP reactor to anisotropically etch the patterned resist through a novolak-like underlayer selective to a Si-containing imaging layer. In this study, both the width and profile control over a range of aspect ratios of a bilayer transfer etch for a 135 nm contact-like deep trench (DT) mask level and a equal line-space (LS) mask printed over severe topography, are examined. Transfer etch studies show that both the profile and the width of the etched feature can be controlled by both the ratio of O@sub 2@/SO@sub 2@ and the bias voltage in the TCP reactor to produce a zero bias vertical profile. The linewidth of the etched feature can be tailored with a positive or negative slope by either decreasing or increasing the ratio of O@sub 2@/SO@sub 2@, respectively, or decreasing or increasing the bias voltage, respectively. As the aspect ratio of the underlayer etch is varied from 5 to 8 in the DT level or as the feature is over-etched by 30%, the linewidth of the etched feature is unchanged. As the lithographic alignment of the LS mask level is incrementally varied with respect to a recessed trench from a previously patterned DT level, the transfer etch can be examined to aspect ratios >10, resulting in a minimum effective width of approximately 25 nm However, at the highest aspect ratios, the trajectory of the transfer etch is observed to be shifted from normal incidence by as much as 45 degrees. Semi-empirical models are used to examine the origin of the altered trajectory of the ions, by determining the relative contribution of ion shadowing from the geometric asymmetry of the transfer into the recess and of the charging effect from thin dielectric films along the sidewall.

4:40pm **PS2-MoA9 Conductor Stack Etching: Technology and Productivity***, **R.A. Gottscho**,* Lam Research Corporation **INVITED**

Conductor etching in the semiconductor industry includes front-end applications such as gate and shallow trench stacks as well as back-end interconnect structures. Future applications center around new materials for gate stacks, to accomodate decreasing voltages and dielectric thickness, and high-k dielectrics, to enable higher density and powerless storage. The technological requirements in gate stack etching center on within wafer critical dimension, CD, control; but, production considerations demand equal attention to wafer-to-wafer, lot-to-lot, and machine-to-machine CD uniformity. For within wafer CD uniformity, gas injection, pumping, plasma generation, and edge ring design all play important roles. However, the aspect ratio variations inherent in circuit design and doping variations within the stack or from stack-to-stack ultimately limit the process window. Waferless cleaning of the chamber and delivered power control provide effective means for minimizing CD variation during large volume production. To preserve the device integrity of ultra-thin gate oxides and maximize yield, novel pre-end-point detection is used with and highly selective over-etch processes. Shallow trench etching mechanisms appear identical to those governing gate stack etching, but by shifting the balance between etching and deposition, trench profiles can be tailored to meet demanding requirements for top rounding, bottom rounding, and side-wall-angle uniformity. In back-end etching, traditional trade-offs remain for resist mask stacks: vertical profiles without residues and charging damage. Hard mask metal etching offers wider process window but at higher cost. The primary focus in the back-end is output, to be gained by increased throughput and longer times between cleans. It is the latter that is driving innovative changes in reactor designs and materials.

Semiconductors
Room 306 - Session SC+EL+SS-MoA

Reactions on Semiconductors

Moderator: R.A. Wolkow, National Research Council of Canada

2:00pm **SC+EL+SS-MoA1 Adsorption of SiH@sub 4@ on Si(001)(2x1) Investigated by Infrared Spectroscopy***, **M. Shinohara**, A. Seyama, Y. Kimura, M. Niwano,* Tohoku University, Japan

Adsorption of silane molecules, SiH@sub 4@ and Si@sub 2@H@sub 6@, onto Si(001) has so far been investigated extensively, because of the potential of using the silane molecules as the source gas for gas source molecular beam epitaxy (GS-MBE) for the growth of Si. Previous studies on Si deposition using silanes have suggested that during the course of Si crystal growth, silanes dissociatively adsorb on Si surface dangling bonds as trihydride (SiH@sub 3@) and dihydride (SiH@sub 2@) species and then decomposes to surface monohydride species, SiH. However, there has been only a little amount of information about the type of hydride species that are generated during the adsorption of silane on Si surfaces. In this study, we used infrared absorption spectroscopy (IRAS) in the multiple internal reflection geometry (MIR) to investigate the adsorption of SiH4 on the Si(001)(2x1) surface. IRAS-MIR provides us with valuable information about the hydrogen bonding configurations on semiconductor surfaces. Comparing infrared data with the density functional cluster calculation, we show that the silane molecule dissociatively adsorbs on Si(001)(2x1) to populate a dihydride (SiH@sub 2@) at the bridge site between two adjacent dimers and a monohydride species; the latter is formed by terminating the unsaturated dangling bonds of dimers by hydrogen atoms that are released from the silane molecule. We found that at high surface hydrogen coverage, surface silyl (-SiH@sub 3@) group and monohydride (SiH) species are generated. We interpret that at high hydrogen coverage, silane adsorbs onto a single dimer that has two unsaturated dangling bonds on which a hydrogen atom and a sylil group (-SiH@sub 3@) stick. We also show that a dihydride species that was initially generated by silane adsorption, dissociates even at room temperature and the released hydrogen atoms migrate on the surface to produce more monohydride species.

2:20pm **SC+EL+SS-MoA2 Si(001):As Gas-source Molecular Beam Epitaxy: As Incorporation and Film Growth Kinetics*, H. Kim,*** University of Illinois*; G. Glass,* PTD, Intel Corp.*; J.A.N.T. Soares,* University of Illinois*; P. Desjardins,* Ecole Polytechnique de Montreal*; J.E. Greene,* University of Illinois

Arsenic-doped Si(001) layers with concentrations C@sub As@ up to 5x10@super 18@ cm@super -3@ were grown on Si(001)2x1 at temperatures T@sub s@ = 575 - 900 °C by GS-MBE using Si@sub 2@H@sub 6@ and AsH@sub 3@. At constant flux ratio, C@sub As@ decreases, while the film growth rate R@sub Si:As@ increases, with T@sub s@. TPD measurements show that As segregates strongly to the growth surface and that the observed decrease in C@sub As@ at high T@sub s@ is primarily due to increasingly rapid arsenic desorption from the segregated layer. Decreasing T@sub s@ enhances As incorporation. However, it also results in lower R@sub Si:As@ due to higher steady-state As surface coverages which decrease the total dangling bond coverage and, hence, the Si@sub 2@H@sub 6@ adsorption rate. At constant T@sub s@, C@sub As@ increases, while R@sub Si:As@ decreases, with increasing AsH@sub 3@ flux. All incorporated As resides at substitutional electrically active sites for concentrations up to 3x10@super 18@ cm@super -3@, the highest value yet reported for Si(001):As growth from hydride source gases. D@sub 2@ TPD spectra exhibit @beta@@sub 1@ and @beta@@sub 2@ peaks associated with Si monodeuteride and dideuteride desorption as well as a new peak @beta@@sub 3@ attributed to desorption from Si-As mixed dimers. Steady-state arsenic surface coverages during film growth, and the As segregation enthalphy, were quantitatively determined as a function of C@sub As@ by comparison with As-adsorbed Si(001) reference samples with known As coverages. From AsH@sub 3@ adsorption kinetics and incorporation data, the AsH@sub 3@ reactive sticking probability on Si(001) was determined and As incorporation kinetics were quantitatively modeled. Initial experiments have demonstrated that temperature-modulated growth can be used to increase both R@sub Si:As@ and C@sub As@ while providing layers which are atomically flat.

2:40pm **SC+EL+SS-MoA3 Scanning Tunneling Microscopy of Impurity Dimers on Hydrogen-Terminated Si(100)-2x1 Surface*, S. Matsuura,*** University of Tokyo, Japan*; M. Fujimori, S. Heike, Y. Suwa, H. Kajiyama, T. Onogi,* Hitachi, Ltd., Japan*; K. Kitazawa,* University of Tokyo, Japan*; T. Hashizume,* Hitachi, Ltd., Japan

We report a new dimer structure on a hydrogen-terminated n-type Si(100)-2x1-H surface found by a scanning tunneling microscopy (STM). The dimer structure is observed almost same as regular surface Si dimers at filled state, at empty state, however, is observed as different structure showing spatial variation of electronic density of states. Similar results were obtained in the case of As-doped surface. The surface density of the structures derived from measurement of the samples with different dopant concentrations was found to be proportional to the dopant density. Electronic structures calculated by first-principles calculations for a phosphorous dimer or an arsenic dimer on the Si(100)-2x1-H surface are in good agreement with the bias dependent STM images of the newly-found structure on the P-doped or As-doped Si(100) surface, respectively. We concluded that the dimer structure represents dopant atoms incorporated on the Si surface and forming a dimer. The calculation also revealed that the surface phosphorous and arsenic atoms are more stable forming dimers than being isolated on the hydrogen-terminated Si surface.

3:00pm **SC+EL+SS-MoA4 Adsorption and Reaction of Fluorinated Fullerenes on Silicon*, Y. Fujikawa,*** *J.T. Sadowski,* Tohoku University, Japan*; K.F. Kelly,* Pennsylvania State University*; K.S. Nakayama, T. Sakurai,* Tohoku University, Japan

The adsorption structure of fluorinated fullerene molecules deposited on silicon was studied using scanning tunneling microscopy (STM) and high-resolution electron energy loss spectroscopy (HREELS). The results of HREELS indicated that the fluorine atoms around the molecules were detached from the molecules and chemisorbed to the surface. These fluorine adsorption sites were directly observed around the adsorbed molecules in the STM images. Some of the fluorine-adsorbed sites were found to form thread-like structures, suggesting that the molecules print the fluorine atoms on the terrace due to the rolling movement of the molecules. Annealing produced different degrees of defluorination of the fullerenes and etching of the silicon surface depending on the temperature. By imaging the intermolecular structure of the molecules with the STM, we can directly observe the loss of the fluorine atoms.

3:20pm **SC+EL+SS-MoA5 STM Study of Self-Assembled Quantum-Dot Arrays of Sn on Si(111)-(7x7) Surface*, M. Yoon,*** *R.F. Willis,* The Pennsylvania State University

The adsorption and diffusion mechanisms of Sn on the Si(111)-(7x7) at sub-monolayer coverages have been studied by scanning tunneling microscopy (STM). It is found that the preference of Sn adsorbates on the faulted-halves of the 7x7 unit cell is dependent on adsorbate coverage up to @THETA@ ~ 0.3 monolayer (ML). At higher coverages (~0.3 - 0.5 ML), the tin atoms cluster together on both halves of the 7x7 unit cell, forming a two-dimensional array of self-assembled quantum dots. This is in contrast to the behavior recently reported@footnote 1@ for Tl condensation on Si(111)-(7x7). In this latter case, the element occupies faulted half-cells preferentially and the surface remains metallic. In the present case, the Sn clusters are semiconducting, the surface showing an energy bandgap which increases with increasing coverage. The surface returns to metallic behavior as the number of Sn atoms approaches that of one monolayer of Si. @FootnoteText@ @footnote 1@L. Vitali, M. G. Ramsey, and F. P. Netzer, Phys. Rev. Lett. 83, 316 (1999).

3:40pm **SC+EL+SS-MoA6 Evolution of Surface Morphology During Sb Growth on Ge(100)*, L.H. Chan,*** *E.I. Altman,* Yale University

Surfactants such as Sb have been found to promote layer-by-layer growth on metal and semiconductor surfaces. It is known that Sb and Ge intermix only at elevated temperature past 630K. Temperature programmed desorption was performed to study the energetics of Sb adsorption on Ge(100). The results demonstrated a typical high temperature peak that saturated at 1020 K before the appearance of a low temperature sublimation peak below 650 K with increasing Sb exposure. An additional high temperature peak at 1070 K was attributed to bulk incorporation of Sb. On a nominal 1 ML Sb covered Ge(100) surface prepared by deposition at 300K and annealing above the multiplayer desorption peak, scanning tunneling microscopy studies showed three surface layers were exposed. The images displayed bias dependent contrast suggesting the layers were not chemically uniform. To address the reasons for the morphology changes and to identify different components on the surface, a systematic study of Sb growth as a function of coverage and temperature was conducted. At room temperature, Sb adsorbs as tetramers and pairs of dimers. Several Sb@sub 4@ adsorption states are identified. Subsequent island growth leads to a poorly ordered surface with short strands of Sb dimer rows. The growth of longer dimer rows was interrupted by the growth of other nearby dimer rows randomly distributed on the Ge surface. Antimony incorporated into the top layer on either annealing or deposition at 600 K. Annealing gave well-structured dimer rows across the surface in all layers. However, intermixing of Sb and Ge at elevated temperature created ad-dimer clusters, vacancy islands, and reattachment of Sb and Ge ad-dimers on the top layer to the step edges. The implications of these results on surfactant-mediated growth will be discussed.

4:00pm **SC+EL+SS-MoA7 Effects of Exposure on GaSe Passivated Si(111)*, J.A. Adams,*** *A. Bostwick, S. Meng, B.R. Schroeder, M.A. Olmstead, F.S. Ohuchi,* University of Washington

GaSe growth on Si(111) 7x7 between 500°C and 550°C results in the formation of a bilayer, which passivates the substrate dangling bonds and serves as the interface for further film growth. Ga sits directly atop surface Si, and the resultant interface bonding leaves Se lone-pair states on the surface, similar to Si(111):As. This makes the Si(111):GaSe surface resistant to contamination, and additional GaSe does not stick for T@sub substrate@@>=@500°C. We have studied the effects of exp osure to various atmospheric constituents on the electronic states and surface structure of the bilayer-passivated silicon surface using x-ray photoelectron spectroscopy and diffraction (XPS/XPD), low-energy electron diffraction (LEED) and ultraviolet photoelectron spectroscopy (UPS). We find that exposure to N@sub 2@ at atmospheric pressure has no apparent effect on the atomic or electronic structure and no N@sub 2@ is found to stick on the surface. However, we find that exposure to atmosphere for 5 minutes does change the surface states as observed from UPS, although LEED shows that the atomic structure of the GaSe bilayer does not change. The surface states can be almost completely recovered upon annealing at 500°C for 1 minute. Exposure to other atmospheric constituents such as O@sub 2@ and H@sub 2@O were also studied.

4:20pm **SC+EL+SS-MoA8 Temporal Changes of Photoemission Spectra of the Alkali-metal-induced Ge(111) 3x1 Surface***, G. Lee,* Korea Research Institute of Standards and Science, Korea*; C. Hwang,* Korea Research Institute of Standards and Science*; Y. Park, S. Cho,* Korea Research Institute of Standards and Science, Korea*; H. Lee,* Korea Research Institute of Standards and Science*; E. Cho,* Chonnam National University, Korea

We investigated the temporal changes of the core-level photoemission spectra of the Ge(111)3x1 reconstructed surface induced by alkali metals (Li and Na) in UHV chamber. It is found that while the spectra from the Ge(111)3x1-Na surface is hardly affected, those from the Ge(111)3x1-Li surface change significantly in time. We identify that the changes of the core-level spectra from the Ge(111)3x1-Li surface are due to the contamination by residual oxygen gas in the chamber. The contamination rate of the Ge(111)3x1-Li surface is even higher than that of the clean surface, contradicting the expectation that alkali-metal-induced 3x1 reconstruction passivates the surface against oxidation. We discuss the difference in the contamination rate between the Ge(111)3x1 surfaces induced by different alkali-metal adsorbates.

4:40pm **SC+EL+SS-MoA9 Role of Excited Electronic States in Reactions on Si(100)***, **J.S. Hess**, D.J. Doren,* University of Delaware

Low-lying excited electronic states of the Si(100) surface can play a role in activated adsorption reactions. The nature of the lowest surface excited state and its coupling to the surface ground state will be described. Density functional theory calculations on cluster models of Si(100) have been used to predict the minimum energy difference between the optimized ground state and first excited state levels. The minimum energy crossing point between the two states was explicitly calculated, as was the spin-orbit coupling between them. The energy needed to reach the excited state surface is low enough, and the coupling between the states is strong enough, that crossing between the two states will be facile. The two states will be in thermal equilibrium and a significant population of the excited state is expected at typical reaction temperatures. The role of the excited state in selected reactions will also be discussed.

5:00pm **SC+EL+SS-MoA10 Dynamics of Photo-induced Reaction on a Chlorinated Si(111) Surface***, **S. Haraichi**, F. Sasaki,* Electrotechnical Laboratory, Japan

In order to study photo-induced reaction of Si/Cl in the low fluence region, which is an influential candidate for low-damage manufacturing at the atomic level, the reaction mechanism was examined in terms of the photo-excitation dynamics using femtosecond second-harmonic generation (SHG). SH signals on a clean 7x7 surface show a rapid dip induced by the pump beam, which is finished within several 100 fs. It is ascribed to charge transfer from the bulk Si to the 7x7 surface and subsequent surface recombination of photo-produced carriers through surface dangling bond states. The rapid dip is not seen on the chlorinated surface, because the surface dangling bond states are disappeared. With the increase of the pump beam power the decay profile of SH signals drastically changes and an upward peak clearly appears on the chlorinated surface. The upward peak is due to the precursor of surface reaction on the Si/Cl system. Though we observed both of photo-excitation SH dynamics on an n-type and a p-type Si surface, the difference was not found. The band bending near the chlorinated surface does not contribute to the reaction dynamics, because it is most likely that the photo-produced carriers immediately flatten the bands. We also observed the reaction dynamics dependence on the pump photon energy. The threshold pump power of the reaction induced by a 1.55 eV pump peam and a 3.1 eV pump beam were 45 mW and 4 mW, respectively. This difference is not only due to an absorption coefficient but also the excitation levels and the relaxation paths, because the upward peak position of SH dynamics was different in two pump photon energy.

Surface Engineering
Room 201 - Session SE-MoA

Coatings for Extreme Environments: Wear Resistant, Lubricious, Anti-corrosive, High Temperature Coatings

Moderator: W. D. Sproul, Reactive Sputtering Inc.

2:00pm **SE-MoA1 Coatings and Surface Engineering for Tough Applications***, **A. Inspektor**,* Kennametal Inc. **INVITED**

A functional surface is an engineered system consisting of substrate and coating designed to work together. From a 50 µm thick diamond layer on cutting tools to a few atoms thin protective barrier on hard drives, a functional surface is a critical component in many new high technology products. It is the first line of defense of the coated part and thus, it is absolutely vital to the performance and to the reliability of the part in tough applications. This paper will present and critically review principles of surface engineering for cutting tools and wear parts. An emphasis will be on the design and preparation of the working surface as illustrated by case studies from diamond-coated cutting tools, thermal barriers for automotive and aerospace engines, concepts in cBN deposition, and recent developments in the field of nano-layer and nano-composite superhard films.

2:40pm **SE-MoA3 Influence of the Interface Composition on the Corrosion Behavior of Unbalanced Magnetron Grown Niobium Coatings on Steel***, C. Schönjahn, **H. Paritong**, W.-D. Münz,* Sheffield Hallam University, UK*; I. Petrov, R.D. Twesten,* University of Illinois, Urbana

In general niobium is well known as a chemically extremely stable material. However the corrosion performance of 0.5 to 1 µm thick , unbalanced magnetron (UBM) grown niobium coatings on steel substrates depends significantly on the in vacuo etching pretreatment of the substrates prior to coating and on the chemical composition of the steel substrate. Corrosion tests, TEM and STEM analyses have shown that a dense fine grained partially implanted 5-10 nm thick niobium interface layer formed during the metal ion etching pretreatment is paramount to protect the steel substrate thoroughly against corrosion in chlorine containing aqueous electrolytes, whereas the pretreatment with Ar @super +@ and Cr @super +@ ions leads to inferior corrosion results. Moreover the energy of the impinging Nb @super +@ ions used during the etching process plays an important role. Maximum pitting potential and minimum corrosion currents were found for bias voltages between -600 and -900 V. In summary the results suggest that the UBM deposited Nb coatings are not completely dense although no evidence for the presence of voids has been found by TEM analysis and that the major justification for niobium as corrosion barrier depends on the existence of the thin interface layer generated by high energetic ion bombardment during the etching step. The UBM deposited coating (U@sub s@=-75V) acts therefore only as an itself chemically stable mechanical spacer protecting the thin interface layer against mechanical damage.

3:00pm **SE-MoA4 Oxidation Resistance of NiAl and NiAl-AlN Coatings Deposited by Magnetron Sputtering***, **D. Zhong**,* Colorado School of Mines*; A.M. Peters,* Los Alamos National Laboratory*; J.J. Moore, G.G.W. Mustoe,* Colorado School of Mines*; J. Disam, S. Thiel,* Schott Glas, Germany

It is well known that NiAl exhibits excellent oxidation resistance and it shows improved cyclic oxidation resistance when NiAl-AlN composite is used. In this work, NiAl and NiAl-AlN coatings have been deposited from a NiAl compound target by using RF magnetron sputtering technique. The oxidation behaviors of NiAl and NiAl-AlN films were studied using a Netzsch Simultaneous Thermal Analyzer (STA409C) and Rutherford Backscattering Spectrometry (RBS). Their structures and microstructures were characterized using x-ray diffraction (XRD), scanning electron microscope (SEM) and transmission electron microscope (TEM). It was shown that they are excellent oxidation resistant coatings. In this paper, their oxidation rates and mechanisms will be discussed together with their structure observations as well.

3:20pm **SE-MoA5 Aspects of Surface Engineering in the Automotive Industry***, **Y.T. Cheng**,* General Motors R&D Center

The manufacturing of an automobile is to a large extent the making of engineered surfaces on several length scales using a variety of processing techniques. In this presentation, we will summarize aspects of our recent work related to surface engineering. Examples include the preparation and characterization of nanocomposite thin films consisting of metal-metal and metal-ceramic materials; their tribological properties and potential application as low-friction and wear resistant coatings for electrical connectors will be discussed. Other examples include the investigation of thin films for sensors, battery electrodes, and catalysts. We will also review our work on modeling indentation measurements. Although significant progress has been made in surface engineering, it is still largely a "trial-and-error" process. We will illustrate with examples the needs for: (1) reducing the cost and improving the reproducibility of tribological coatings, (2) better characterization techniques for mechanical property measurements at the nano- and micro-meter scales, and (3) design guidelines and models based on the fundamental understanding of the relationships between the structure, property, and performance of engineered surfaces.

3:40pm **SE-MoA6 Tribological Performance and Initial Finite Element Modeling of Reactively Sputtered Single and Multi-layer Chromium Nitride Thin Films***, **S.L. Rohde**, L. Olson, S.M. Aouadi,* University of Nebraska*; D.M. Mihut,* Multi-Arc Scientific Coatings*; B. Neville,* Iowa State University*; D.M. Hornyak,* University of Nebraska

Tribological properties of Cr-N based single- and multi-layer thin films are compared with FEA modeled stress fields under similar loading, to evaluate the feasibility of "building-in" load support, with alternating hard/soft film layers to optimize performance on both traditional tool steels and more compliant substrates. The first phase involved the deposition and evaluation of coatings on substrates of both hardened A2 tool steel and 2024-alloy aluminum. Next, the wear behavior was assessed using pin-on-disk (PoD) tests, performed unlubricated at 40 to 50% humidity using alumina and/or tungsten carbide 'pins'. The wear was reduced in most cases, with the multi-layered structures performing best on all substrate materials. PoD tests on the A2 tool steel substrates, favored the hardest thin film structures; however, these same films did not perform as well on the more compliant Al-substrates. For the Al-substrates, neither the stiffest nor the most compliant films excelled, instead multi-layer films with alternating hard/soft structures designed to provide a more graded compliance from the substrate up to the rigid top layer yielded the best results. In this case, wear rates were reduced by as much as much as three orders of magnitudes over uncoated 2024 Al. In the final stage, finite element modeling studies have been initiated to try to understand the behavior of these multilayered coating/substrate combinations under specific loading conditions. First generation models are matched to their respective wear systems and the results compared. These models will then be used to guide the development of second generation coatings, that will be used to verify and improve the efficacy of the models. The goal of the modeling program is thus to facilitate specification and optimization of application specific coating structures into the original component designs.

4:00pm **SE-MoA7 Tribological Performance of a Novel High Wear Resistant 390 Al Alloy Overlay***, **R.D. Ott**, C.A. Blue, M.L. Santella, P.J. Blau,* Oak Ridge National Laboratory

A novel process has been developed at Oak Ridge National Laboratory (ORNL) for the production of high silicon (Si) containing aluminum (Al) alloy surface layers (overlay) on Al alloys. The main purpose of the overlay is to improve the wear resistance of the underlying alloy. The process is versatile enough to place the overlay only in critical areas, thus, greatly reducing the cost of a component. Instead of manufacturing a component from expensive high Si content 390 Al alloy, the component could be manufactured from an inexpensive alloy, such as 319 Al alloy, and the 390 Al alloy overlay could be placed in essential areas were high wear resistance was required. Test specimens comprising of 390 Al alloy overlays on 319 Al alloy have been processed to mimic bulk 390 Al alloys. Pin-on-disk wear tests have been performed, following ASTM standards, to quantify the wear resistance of the 390 Al alloy overlay with that of bulk 390 Al alloy. Wear tests have also been performed on bulk 319 Al alloy as a baseline. Lubricated and non-lubricated pin-on-disk wear tests were conducted utilizing 440C stainless steel and 52100 steel balls as the pin material. Also evaluated were the frictional forces during the wear tests, scratch hardness, microhardness, and the Hertzian contact pressures. From the tests conducted, the 390 Al alloy overlay shows potential as a replacement of bulk 390 Al alloy for high wear resistant applications.

4:20pm **SE-MoA8 Mechanical and Tribological Properties of Substoichiometric Oxide and Superstoichiometric Carbide Coatings for Wear Reducing and Lubricating Applications***, **St. Bärwulf**, E. Lugscheider, K. Bobzin,* University of Technology Aachen, Germany

The tungsten and vanadium oxides are promising to be usable as solid lubricants at elevated temperatures because of their ability to form non stoichiometric Magnéli-phases with reduced shear strength. So far they were mainly investigated as powdery material or as a component of ceramics for tribological or machining applications. As a matter of fact metal-oxides are interesting for tribological insets at atmospheric conditions because of their expected oxidation stability, hardness and low adhesion against the counterbody. For low temperature insets carbon containing coatings are meanwhile widely spread in numerous applications. Because of their phase generation / transition the zircon- and hafnium-carbon systems offer a very interesting possibility to deposit graded coatings with self-adapting properties in dependance on the external mechanical load and the contact conditions. This self-adapting effect will be shown exemplarily for a hydraulic component after an inset under load in relative motion. The presentation will report about the mechanical and tribological properties of these coatings. Further possible ranges of applications will be deduced from the fundamental characterization and results of concrete insets (e.g. machining) shown. Therefore the coatings were analyzed by various testing methods to characterize the tribological, mechanical and structural properties, like contact angle measurements, SEM, scratch testing, nanoindentation, XRD and pin on disk.

4:40pm **SE-MoA9 Thin Film Disk Contact Start/stop Durability Failure Model: Subcritical Interfacial Crack Growth***, **R.L. White**, V. Raman,* IBM Corporation

Analogous to fatigue failure in bulk materials, contact start/stop (CSS) failure of thin film disks is modeled as the progressive growth of interfacial cracks resulting from the cyclic tractions applied by intermittent slider-disk contact. Interfacial cracks eventually reach a critical dimension, resulting in film fracture or spallation and catastrophic failure of the head-disk interface. There are two bodies of evidence which support such a model. The first derives from scratch adhesion testing of mechanically textured disk media. The scratch data demonstrate that the same weibul statistics that can be fitted to CSS failures also describe the distribution of critical loads necessary to produce delamination of the disk metallurgy. Furthermore, a number of cases can be cited in which the critical loads can be correlated to start/stop durability, including the effects of hydrogenation on the start/stop durability of CHx overcoats. Secondly, this model provides for the semi-quantitative prediction of the effects of head-disk interface parameters which are in general agreement with empirical studies. The tractions applied at the head-disk interface are predicted to diminish with distance from the interface with a 1/d dependence. Since subcritical crack growth rate follows a power law relationship to stress intensity, start/stop failure statistics would be expected to show a power law dependence on carbon thickness. Data are presented demonstrating CSS life is proportional to the 3rd power of carbon thickness. The effects of CSS test temperature and slider size can also be rationalized based on the above model for CSS failure.

Surface Science
Room 208 - Session SS1-MoA
Model Catalysts at High Pressures

Moderator: A.G. Sault, Sandia National Laboratories

2:00pm **SS1-MoA1 A New Mechanism for Hydrocarbon Dehydrogenation on Pt under Conditions of High Hydrogen Coverage***, J.C. Hemminger,* University of California, Irvine*; **D.A. Perry**,* University of Illinois

In 1978 Demuth and Ibach published the HREELS vibrational spectrum of cyclohexane (C_6H_{12}) adsorbed on clean Pt(111) at low temperature showing strong softening of some C-H modes. Subsequently, data from several laboratories resulted in a consistent picture for the initial step in the dehydrogenation of cyclohexane on clean Pt. The mechanism of the dehydrogenation involves the weakening of one of the axial C-H bonds of the cyclohexane by interaction with a Pt 3-fold hollow site (leading to the soft C-H modes). This is followed by C-H bond breaking to form Pt-H and Pt-C bonds. The initial dehydrogenation product is cyclohexyl (C_6H_{11}). Work from our laboratory has shown that in the presence of high coverages of surface hydrogen the dehydrogenation actually occurs at a lower surface temperature, indicative of a 20% reduction in the activation energy for the initial step. In combination with our HREELS data, that shows no C-H mode softening, this reduction of the activation energy strongly indicates a different mechanism for the dehydrogenation in the presence of high surface coverages of hydrogen. The high surface coverages of hydrogen will effectively fill the 3-fold hollow sites on Pt(111). This leads to a more weakly adsorbed cyclohexane and the lack of softening of the C-H modes. Under these conditions we propose that the dehydrogenation occurs via a σ bond metathesis mechanism. In this mechanism, which is well established in metal-hydride organometallic chemistry, a hydrogen that is bonded to the Pt interacts strongly with a hydrogen of the cyclohexane. The metal-hydride hydrogen combines with the hydrogen from the cyclohexane to directly form H_2 at the same time that a C-Pt bond is formed. This concerted mechanism is consistent with our observations that the C-H modes are not softened when the 3-fold hollow sites are blocked with hydrogen and yet a lower activation barrier path to the initiation of the dehydrogenation exists.

2:20pm **SS1-MoA2 The Role of Surface Hydrocarbon Species during Palladium-Catalyzed Reactions at High Pressures***, **D.J. Stacchiola**, W.T. Tysoe,* University of Wisconsin, Milwaukee

It now appears clear that many, if not all, transition-metal-catalyzed hydrocarbon conversion reactions proceed in the presence of a relatively strongly bound carbonaceous layer adsorbed on the surface of the catalyst. In the case of Pd, ethylidyne species are present during ethylene hydrogenation, and vinylidenes in the case of reactions involving acetylene. In order to investigate adsorption on these carbonaceous-layer-covered surfaces, we have studied the adsorption of small molecules on both an ethylidyne-covered and a vinylidene-covered Pd(111) surface using molecular beam strategies and infrared spectroscopy under high pressure conditions. Results on the influence of carbonaceous layers on the hydrogenation kinetics of small hydrocarbons under high pressures are also discussed.

2:40pm **SS1-MoA3 Effect of the Environment on the Surfaces of Metals and Metal Oxides***, **M. Scheffler**,* Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany **INVITED**

Surface Science UHV studies, in particular when concerned with metals or metal oxides, in some sense often investigate an artificial state. This means, the surface stoichiometry, and as a consequence the electronic properties, of the studied systems are significantly different to those that would exist in a realistic environment, which typically contains oxygen and water at higher pressure and temperature. This talk summarizes concepts for describing how the pressure and temperature of the environment or atmosphere affect surfaces.@footnote 1-3@ --- I will also describe recent developments in methodology: By combining density functional theory calculations with a lattice-gas Hamiltonian approach and the kinetic Monte Carlo method, surface phenomena can be described over time scales of the order of seconds and length scales of the order of micron.@footnote 4,5@ Examples of such calculations consider long-ranged adsorbate-adsorbate interactions,@footnote 5@ island formation and crystal growth, as well as surface structures with disorder, and thermal desorption.@footnote 4@ --- Using Ru as the main example (but also mentioning Al, Cr, Fe, Rh, Ag) I will show that the interaction with an oxygen atmosphere gives rise to a dramatic restructuring of the surface, yielding to mesoscopic domains of different stoichiometry and very different chemical activity.@footnote 1, 6-8@ The results will be discussed in view of their possible relevance for oxidation catalysis. --- @FootnoteText@@footnote 1@X.-G. Wang et al., Phys. Rev. Lett. 81, 1038 (1998). @footnote 2@ X.-G. Wang, A. Chaka, and M. Scheffler, Phys. Rev. Lett. 84, 3650 (2000). @footnote 3@ X.-G. Wang and M. Scheffler, to be submitted to Phys. Rev. B. @footnote 4@C. Stampfl et al., Phys. Rev. Lett. 83, 2993 (1999). @footnote 5@K.A. Fichthorn and M. Scheffler, Phys. Rev. Lett., May (2000). @footnote 6@A. Böttcher, H. Conrad and H. Niehus, J. Chem. Phys. 112, 4779 (2000). @footnote 7@ A. Böttcher et al., submitted to Surf. Sci. Lett. @footnote 8@H. Over et al., Science 287, 1474 (2000).

3:20pm **SS1-MoA5 Low Temperature CO Oxidation on the Pt(111) Surface Studied Over an Extended Pressure Range***, **D.J. Burnett**, A.M. Gabelnick, A.T. Capitano, A.L. Marsh,* University of Michigan*; D.A. Fischer,* National Institute of Standards and Technology*; J.L. Gland,* University of Michigan

In-situ Fluorescence Yield Soft X-ray methods and Temperature Programmed Reaction Spectroscopy (TPRS) experiments were used to characterize the oxidation of CO in the temperature range where molecular oxygen dissociates. Taken together, these experiments enable characterization of this reaction over an extended pressure range (UHV to 0.01 Torr). Coadsorbed molecular oxygen and carbon monoxide TPRS experiments show that molecular oxygen must be adsorbed prior to carbon monoxide in order for low temperature (145 K) carbon dioxide to be produced. When molecular oxygen is preadsorbed with CO, the leading edge of molecular oxygen desorption is lowered nearly 20 degrees with a shoulder emerging at 127 K. When CO is preadsorbed, the molecular oxygen desorption peak remains unchanged (single peak with maximum at 142 K). Temperature Programmed Fluorescence Yield Near Edge Spectroscopy (TP-FYNES) experiments, capable of monitoring reactions under reactive atmospheres, were performed in pressures up to 0.01 Torr. For preadsorbed molecular oxygen with a CO overlayer, the same amount of low temperature carbon dioxide is formed when heated in vacuum and in oxygen pressures up to 0.002 Torr. For preadsorbed partial CO monolayers, the low temperature CO oxidation channel can be reached using pressures of oxygen (0.0005 to 0.01 Torr), as opposed to UHV experiments. Based on these results, oxygen dissociation appears to be limited in the vicinity of CO. Since coadsorbed CO enhances molecular oxygen desorption, these results suggest that competition between desorption of molecular oxygen and dissociation limits the reaction with coadsorbed CO. Detailed isothermal kinetic studies were performed with preadsorbed CO to establish a more detailed understanding of the oxidation mechanism.

3:40pm **SS1-MoA6 Rapid Reactions on Nanofabricated Catalyst Pt Particles***, **L. Österlund**, S. Johansson, B. Kasemo,* Chalmers University of Technology, Sweden

The CO oxidation steady-state kinetics has been measured at atmospheric pressure on nanofabricated catalysts. The Pt/ceria and Pt/SiO@sub 2@ catalyst samples used in the present study were prepared by electron-beam lithography (EBL) technique as previously described.@footnote 1@ This technique offers unprecedented opportunities of preparing catalyst particles of well-defined size distribution. Simultaneously it opens the possibility of independently changing particle size, inter-particle distance and the interface between different components, respectively. Here we report results on fairly large, polycrystalline particles (700 nm diameter), as well as smaller crystalline particles formed by disintegration of Pt particles at well-controlled exposures to a H@sub 2@/O@sub 2@ gas mixture.@footnote 2@ The reaction kinetics of the CO oxidation, including the kinetic phase transition and the bistability region has been explored in detail theoretically.@footnote 3@ However, experimental results at high pressures are still by and large lacking. The results presented here fills this gap and provides new information of the kinetic parameters governing the reaction. Rapid reactions on nanometer particles can be very different from those on an infinite surface. Results of the reaction kinetics on the small Pt particles are discussed in this context . @FootnoteText@ @footnote 1@ S. Johansson et al. J. Vac. Sci. Technol. A 18, No 4 (2000). @footnote2@ K. Wong, S. Johansson, and B. Kasemo, Faraday Discuss. 105, 237 (1996). @footnote 3@ V. P. Zhdanov and B. Kasemo, Surf. Sci. Rep. 20, 111 (1994).

4:00pm **SS1-MoA7 Co-adsorption and Reaction of Ethylene and NO over Rh Loaded Ceria Surfaces***, D.R. Mullins, **S.H. Overbury**,* Oak Ridge National Laboratory

In ceria containing emission control catalysts, such as three-way convertors in automobiles, the ceria plays an important role in oxygen exchange in both reduction and oxidation reactions. It is important to understand this role in catalytic reaction pathways. We have used soft x-ray photoelectron spectroscopy and TPD to study the co-adsorption and reaction of ethylene and NO on model catalysts surfaces composed of Rh deposited onto ceria films of controlled oxidation state. Studies focused on the effect of the oxidation state of the ceria upon the reaction pathways. The reactions occur predominantly on the Rh particles but are affected by oxygen spillover, interfacial reactions and modulation of the Rh reactivity by the ceria. Following adsorption at 100 K and subsequent programmed temperature increase, the ethylene decomposes in stages on the Rh particles leading to hydrogen evolution and leaving a reactive C species capable of reducing the ceria to produce CO. Correspondingly, NO reacts with both Rh and ceria. NO oxidizes the ceria resulting in N@sub 2@ evolution. NO dissociation occurs on Rh to an extent dependent upon the oxidation state of the ceria support. There is little interaction between co-adsorbed NO and ethylene when the ceria support is fully oxidized, except for site competition on Rh at low temperature. As temperature is increased water and N@sub 2@ are evolved followed by higher temperature CO evolution. However, for highly reduced ceria, water desorption is eliminated in favor of H@sub 2@, due to oxygen spillover onto ceria. Also, there is strong interaction between the N and C species on Rh which stabilizes them with respect to evolution of CO and N@sub 2@. Except for the absence of isocyanate and the presence of hydrogen and its branching between H@sub 2@ and water, the results are similar to reactions between CO and NO. Research sponsored by the Division of Chemical Sciences, Geosciences, and Biosciences, USDOE.

4:20pm **SS1-MoA8 Reducibility of Model Catalytic Converter Oxygen Storage Materials: Thin Ce@sub x@Zr@sub 2-x@O@sub 2@(111) Films Grown on Y-Stabilized Zirconia Single Crystals***, **C.H.F. Peden**, T. He, G.S. Herman,* Pacific Northwest National Laboratory*; Y.-J. Kim,* Taejon National University of Technology*; Y. Gao, S. Thevuthasan,* Pacific Northwest National Laboratory

Dramatic improvements have been made in automobile exhaust converter catalysts by the incorporation of oxygen storage (OS) materials, usually consisting of ceria (CeO@sub 2@) or modified ceria, that can effectively damp deviation in the exhaust air/fuel (A/F) ratio bringing the gas phase closer to the stoichiometric point. We have been growing and characterizing thin films of CeO@sub 2@ and ceria-zirconia (Ce@sub x@Zr@sub 2-x@O@sub 2@) for use as model materials for fundamental studies of their oxygen uptake, storage, and release properties. In this presentation, the growth and characterization (by x-ray diffraction, atomic force microscopy, reflection high-energy electron diffraction, low-energy electron diffraction, x-ray photoelectron spectroscopy (XPS) and diffraction, and low-energy ion scattering spectroscopy) of model CeO@sub 2@ and Ce@sub x@Zr@sub 2-x@O@sub 2@ thin films will be presented. A wide range of growth parameters using oxygen plasma-assisted molecular beam epitaxy have been used, and successful production of pure-phase, single-crystalline epitaxial oxide films has been achieved. We will also report results of XPS and temperature-programmed desorption experiments that have probed the rates of oxygen incorporation and removal from these materials. In particular, we have found that doping of the CeO@sub 2@ by Zr markedly enhances the kinetics of these processes.@footnote 1@ @FootnoteText@ @footnote 1@Pacific Northwest National Laboratory is a multiprogram national laboratory operated for the U.S. Department of Energy by Battelle Memorial Institute under contract number DE-AC06-76RLO 1830.

4:40pm **SS1-MoA9 Mocart: A Tool for Simulation of Heterogeneous Reactions Systems by a Monte-Carlo Method**, *R. Kissel-Osterrieder, **F. Behrendt**, J. Warnatz,* Universität Heidelberg, Germany

A general purpose program called mocart for dynamical Monte-Carlo simulations of catalytic surface reactions has been developed. The stochastic model is based on the Master equation. Inputs for the program are the catalytic surface and its structure, the adsorbates and their initial distribution, the elementary reaction steps and their rate coefficients, and the adsorbate-adsorbate interactions, which can be defined for a variety of systems. The Monte-Carlo program is embedded in a computational fluid dynamics code for simulation of stagnation flow fields directed towards a reactive surface. Various aspects of performance improvements are discussed for three applications of this code. These cover the effects of defect sides on the evolution of reaction waves, the formation of spatio-temporal pattern, and models systems for supported catalyst. For all cases, the numerical results are compared with experimental observations.

5:00pm **SS1-MoA10 In Situ Soft X-ray Studies of CO Oxidation on Pt(411): Studies of Defect Reactivity**, ***H.D. Lewis**, D.J. Burnett, A.M. Gabelnick, J.L. Gland,* University of Michigan*; D.A. Fischer,* National Institute of Standards and Technology

The oxidation of preadsorbed CO on a Pt(411) single crystal surface has been studied over a temperature range of 100 to 600 K and in oxygen pressures up to 0.002 Torr using temperature-programmed fluorescence yield near-edge spectroscopy (TP-FYNES) above the carbon K edge. CO desorption from the Pt(411) surface shows that two-site desorption from step and terrace sites occurs. CO desorbs from terrace sites at 365 K and at 460 K from step sites, showing that CO is more strongly bound at the step sites. At low oxygen pressures (10@super-7@ Torr) oxidation occurs in two steps, beginning at terrace sites and then proceeding to step sites. At higher oxygen pressures (10@super-4@ Torr), one step oxidation at both the terrace and step sites is observed. Measuring surface carbon concentration it was determined that 60% of the CO adsorbed on the Pt(411) surface was on step sites, while the remaining 40% occupied the terrace sites. Isothermal kinetic studies were performed to establish a more detailed understanding of the oxidation mechanism. Kinetic parameters obtained in high oxygen pressures compare favorably to those on the Pt(111) surface.

Surface Science
Room 209 - Session SS2+EL-MoA
Electronic Structure and Excitations

Moderator: R.A. Bartynski, Rutgers University

2:00pm **SS2+EL-MoA1 Recent Photoemission Studies of Quasi-1D Solids**, ***K.E. Smith**, J. Xue, L.C. Duda,* Boston University*; A. Fedorov, P.D. Johnson,* Brookhaven National Laboratory*; W. McCarroll, M. Greenblatt,* Rutgers University **INVITED**

Much controversy surrounds the interpretation of the results of angle resolved photoemission spectroscopy (ARP) studies of the electronic structure of quasi one-dimensional (1D) solids. In principle, ARP should provide valuable information about quasi-1D solids, including the structure of the Fermi surface and possible non-Fermi liquid behavior of electrons close to the Fermi level (E@sub F@). In practice, straightforward interpretation of the spectra is often difficult. It has been reported that photoemission from states near E@sub F@ in quasi-1D conductors differs significantly from that measured from two and three dimensional solids. There are a number of possible explanations for these observations, including problems with surface defects and stoichiometry, charge density wave fluctuations leading to a pseudogap, or a Luttinger liquid state. We report here the results of a temperature dependent ARP study of the electronic structure close to E@sub F@ in the quasi-1D conductors Li@sub 0.9@Mo@sub 6@O@sub 17@ and K@sub 0.3@MoO@sub 3@.@footnote 1@ These materials are ideal for ARP studies since large high quality crystals can be grown, and surfaces suitable for ARP measurements can be prepared by cleaving in vacuum. Using very high momentum and energy resolution ARP, we clearly measured for both materials: i) quasi-1D bands dispersing across the Fermi surface; ii) substantial emission intensity at E@sub F@ in the metallic phase; and iii) a gap opening at E@sub F@ as the samples are cooled through the metal-semiconductor transition. Our results differ from many earlier ARP studies of quasi-1D solids. The differences are likely due to an order of magnitude improvement in angular resolution (and corresponding improvement in momentum resolution) for the spectrometer used here. The reported non-Fermi liquid behavior in photoemission from these solids will be discussed. @FootnoteText@ Supported in part by the DOE under DE-FG02-98ER45680 (KES) and DE-AC02-98CH10886 (PDJ).

2:40pm **SS2+EL-MoA3 Fermi Contours and Adsorbate Phonon Anomalies for Li/Mo(110) and Li/W(110)**, ***E. Rotenberg**,* Lawrence Berkeley National Laboratory*; S.D. Kevan,* University of Oregon

Angle-resolved photoemission was used to measure the Fermi contours of surface-localized states on the Mo(110) and W(110) surfaces with varying amounts of adsorbed lithium up to 1 ML. In analogy with recent results for H on Mo and W(110), we find that the contours are well nested and therefore can drive a surface phonon anomaly. The nesting vector parallel to the @Sigma@ azimuth on Mo(110) at monolayer coverage is in good agreement with recent phonon measurements.@footnote 1@ We also report the variation of this nesting vector as a function of coverage, and show that a more complete understanding of the electron-phonon coupling on these surfaces might be obtained from coverage-dependent measurements of surface phonon dispersion relations. Finally, our results suggest even better nesting along the @Gamma@ --> S direction and that a more pronounced anomaly might be observed there. @FootnoteText@ @footnote 1@J. Kroger, D. Bruchmann, S. Lehwald, and H. Ibach, Surface Science 449(1-3),227 (2000).

3:00pm **SS2+EL-MoA4 Thickness Dependence of the Unoccupied Electronic States in the Pd/Ru(0001) System**, ***W.-K. Siu**, T. Mensing, R.A. Bartynski,* Rutgers University

The unoccupied electronic structure of the Pd/Ru(0001) system has been examined using inverse photoemission spectroscopy for Pd thicknesses in the 1 - 15 monolayers range. Previous studies indicate that in the sub-monolayer coverage range, the desorption temperature of CO on Pd/Ru(0001) is less than that of CO/Pd(111) or CO/Ru(0001). Similarly, we have previously shown that the desorption temperature for CO from the Cu/fccCo/Cu(100) metallic quantum well (MQW) system is a non-monotonic function of film thickness and is correlated with MQW states crossing the Fermi level. This suggests that quantum size effects can influence the strength of the chemisorption bond. As Pd interacts more strongly with CO, our objective is to investigate the occurrence of MQW states in the Pd/Ru(0001) system and determine their influence in CO chemisorption. Metallic quantum well (MQW) states are observed at the @Gamma@ point of the Pd thin film. The energies of these states change as a function of the film thickness. A simple phase accumulation model provides a semiquantitative understanding of this behavior. There is also an unoccupied surface state at @Gamma@, which shifts to higher energy with increasing film thickness, approaching that of the single crystal Pd(111) surface state. We have also determined the energy dispersion with parallel momentum of the unoccupied Pd states along the @Gamma@K and @Gamma@M directions. Finally, the influence of MQW states on the adsorption of CO on the Pd/Ru(0001) system will be discussed.@footnote 1@ @FootnoteText@ @footnote 1@ Supported by NSF-DMR #98-01681 and ACS-PRF #33750-AC6,5.

3:20pm **SS2+EL-MoA5 High Resolution Photoelectron Spectroscopy of Pu at the Advanced Light Source**, ***D.A. Arena**, J.G. Tobin,* Lawrence Livermore National Laboratory*; D. Shuh, E. Rotenberg,* Lawrence Berkeley National Laboratory*; J. Terry, R.K. Schulze, J. Lashley, T. Zocco, D. Farr,* Los Alamos National Laboratory

High resolution photoelectron spectroscopy of Pu has been performed at the Spectromicroscopy Facility (Beamline 7.0) at the Advanced Light Source in Berkeley. Based upon an initial analysis of the data, two key results are immediately obvious. (1) The 5d-5f Resonant Photoemission of the Pu 5f levels exhibits a dependence upon the Pu phase and structure. For example, the results from alpha and delta Pu differ significantly. This strongly suggests that electronic behavior is linked to atomic ordering and structure in Pu. (2) Contamination with oxygen and carbon may be more insidious and subtle than initially believed. Photoemission measurements at a photon energy of 800eV exhibit oxygen and carbon core level peaks, while the same sample shows no contamination utilizing a photon energy of 1253eV, a typical laboratory source energy used in ECSA machines (i.e., Mg k-alpha). In other words, what was thought to be "clean" may not have been. Furthermore, contamination issues like these have a crucial impact upon interpretation of Pu core level spectra, e.g. localized and delocalized screening by 5f electrons. Additionally, 5f-6p Resonant Photoemission, core level spectra (particularly the Pu 4f's) and X-Ray absorption data, all from the Pu will be presented and discussed. Future plans, including ideas about studying magnetic effects in Pu, will also be described. UCRL-JC-133518 Abs.

3:40pm **SS2+EL-MoA6 Plasmon Resonance Spectroscopy of Plutonium Metal Allotropes***, **R.K. Schulze**, J.D. Farr,* Los Alamos National Laboratory

We have measured the plasmon resonance response of the cleaned and well characterized surfaces of the six plutonium thermal allotropes (@alpha@, @beta@, @gamma@, @delta@, @delta@', @epsilon@) using backscatter electron energy loss spectroscopy (EELS). The energy of the plasmon resonance is highly dependent upon the electronic structure of the solid surface, and in particular, the density of electrons available for conduction. Using this method we probe directly, for the first time, the number of free electrons, and the changes in the electronic structure of the plutonium. EELS spectra were acquired on a high purity sample of plutonium with primary electron beam energies of 150, 200, 500, 700, and 1000 eV, and with the sample at seven different temperatures: -125 (@alpha@), 45 (@alpha@), 156 (@beta@), 250 (@gamma@), 410 (@delta@), 465 (@delta@'), and 525°C (@epsilon@). Changes in the plasmon resonance spectra over the 150 to 500 eV primary beam energy range indicate that a surface reconstruction exists for each of the Pu allotropes. The 700 and 1000 eV EELS measurements are alike, indicating that bulk characteristics are being probed at these energies. The bulk plasmon resonance energies for the allotropic series (@alpha@, @beta@, @gamma@, @delta@, @delta@', @epsilon@) are 12.23, 11.18, 11.16, 10.81, 10.94, and 10.92 eV. From these measurements, we extract the volume density of free electrons in each allotrope. In electrons per nm@super 3@ these are, for the series, 108.5, 90.7, 90.3, 84.8, 86.8, and 86.5. These results correlate directly with measurements of resistivity and magnetic susceptibility for the series of allotropes, indicating that the changes in free electron density are identically responsible for the changes in these physical properties. The implications of these results in terms of the electronic properties of Pu and in the changes of electronic structure between the allotropes will be discussed.

4:00pm **SS2+EL-MoA7 Lifetimes of Conduction Band States at Semiconductor Surfaces***, **Th. Fauster**, M. Kutschera, C. Kentsch, M. Wiets, I.L. Shumay, M. Weinelt,* University Erlangen, Germany

In time-resolved two-photon photoemission electrons are emitted after absorption of two photons. By a suitable delay between the two photons the lifetimes of conduction band states can be directly measured in pump-probe experiments. Using time-resolved two-photon photoemission we have studied several semiconductor surfaces. On the Si(100)-(2x1) surface several bulk and surface transitions with unoccupied intermediate states between the conduction band minimum and the vacuum energy are observed. Below the conduction band minimum we find a lifetime in the ps range, which we attribute to the unoccupied surface state. This unoccupied as well as the occupied surface state which originate from the silicon dangling bonds are clearly resolved within the same experiment. On epitaxial, metallic CoSi@sub 2@(111) films on a Si(111)-substrate three unoccupied states could be identified. Their lifetimes lie in the 10 fs range. Neither the lifetimes nor the energetic positions of those unoccupied states depend on the film thickness. On the SiC(0001)-(@sr@3x@sr@3)R30° surface the occupied and unoccupied Mott-Hubbard surface bands are observed. An asymmetric splitting relative to the Fermi level is found in agreement with recent theoretical calculations.

4:20pm **SS2+EL-MoA8 Oscillating Band-bending at the Initial Stage of Sb Growth on Si(100) held at 60K***, **J.M. Seo**,* Chonbuk National University, Korea

Using the synchrotron photoemission spectroscopy, the band-bending, the work-function and the valence band edge were simultaneously monitored at the initial stages of Sb growth on Si(100) held at 60 K. By the intensity attenuation of Si 2p with increasing Sb coverage, it can be deduced that Sb forms a relatively uniform overlayer on Si(100) at 60 K. The band-bending, determined by the bulk Si 2p position, oscillates within 0.15 eV up to about 4 ML of Sb, while the corresponding work-function, monitored by the secondary-cutoff position of biased substrate, negligibly changes. The metallicity, monitored by the valence band edge, indicates that the surface becomes semiconductor-like up to about 1.5 ML but recovers its metallic character with additional Sb coverage. These results implicate that the oscillating band-bending is due to the local charge exchange between the dimer row and Sb at the interface, while the corresponding metallicity of Sb film is determined by the amount of confined and available charges within the film.

Surface Science
Room 210 - Session SS3-MoA
Surface Diffusion and Wetting

Moderator: E.D. Williams, University of Maryland

2:00pm **SS3-MoA1 Theory of Surface Electromigration on Heterogeneous Metal Surfaces***, **P.J. Rous**,* University of Birmingham, U.K., UK

We report a calculation of the magnitude and direction of the wind force for the self-electromigration of adatoms on heterogeneous metal surfaces. Using layer-KKR and jellium methods we have computed the wind valence of adatoms interacting with adatom islands and voids on the low Miller index surfaces of several simple and noble metals. In the vicinity of an island, we find that the magnitude and direction of the electromigration driving force is significantly different from the force felt by an isolated adatom on a large terrace. Therefore, the usual assumption that driving force in surface electromigration is uniform and isotropic is shown to be inaccurate. Using the results of these calculations as input to kinetic Monte-Carlo simulations, we explore how this inhomogeneity of the wind force is manifest in the driven surface diffusion of adatom islands on a current-carrying metallic substrate.

2:20pm **SS3-MoA2 Direct Measurement of Long Jumps of Pd on Cu(001) using Atom-Tracking STM***, **B.S. Swartzentruber**,* Sandia National Laboratories*; M.L. Grant, J.B. Hannon,* Carnegie Mellon University

When Pd atoms are deposited onto a Cu(001) crystal surface, they readily place exchange with the surface Cu atoms, forming a 2-d surface alloy phase. At low coverage, Pd atoms are distributed randomly in the surface layer. At coverages approaching 0.5 ML, an ordered (2x2) alloy phase forms. The kinetic processes by which the incorporated Pd atoms form ordered structures are currently poorly understood. Using atom-tracking STM, a technique in which the probe tip is locked onto the diffusing species using lateral, XY, feedback, we have directly measured the diffusion of the Pd atoms as a function of temperature. The position of individual Pd atoms is recorded as a function of time with millisecond time resolution, thus recording the diffusion path of the incorporated atom. From these data, the relative binding energies of the sites visited by the atom, as well as the local diffusion barriers, are determined. We find that a large percentage (~25%) of the diffusion events involve displacements that are greater than a single lattice spacing - so-called long jumps. The distribution of jump lengths is well described by a process in which a Pd atom is thermally activated to a metastable binding-energy state, perhaps to a site on the surface, where it can perform several unit-length hops before it comes to rest in another stable binding site. Measuring the details of this atomistic process allows us to better understand the formation, growth, and mass transport kinetics of binary surface alloy structures. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the US-DOE under contract DE-AC04- 94AL85000.

2:40pm **SS3-MoA3 Bronze Formation through the Motion of Tin Islands on Cu(111)***, **A.K. Schmid**, N.C. Bartelt, R.Q. Hwang,* Sandia National Laboratories

When Sn atoms are deposited on top of a Cu (111) surface at room temperature, they exchange into the surface to form a surface bronze alloy. One might have expected that this process would be rather simple, the understanding of which would be largely complete when one understood how a single Sn atom exchanged with a single Cu atom. We find, however, that the alloying occurs by an entirely unanticipated cooperative process that is considerably more intriguing than this. Using a combination of atomic resolution scanning tunneling microscopy (STM) and low-energy electron microscopy (LEEM) we find that shortly after Sn deposition large, 100,000 atom 2-D Sn islands coalesce on the Cu surface. These islands proceed to run across the surface. As they move, Sn atoms within the islands randomly exchange with Cu atoms in the surface. The exchanged Cu atoms are ejected from the Sn islands in the form of ordered 2-D bronze crystals. Sn islands consistently move away from their trail towards unalloyed regions of the Cu surface. We are able to trace the motion of the Sn islands to a simple atomic fact: Sn atoms on top of the Cu surface are strongly repelled by Sn atoms already incorporated into the Cu. The islands thus lower the free energy of the surface by moving. We find that island velocity is independent of size, consistent with a model in which the mobility of the Sn islands is determined by diffusion through the interior of the islands.

3:00pm **SS3-MoA4 Low Energy Electron Microscope Investigations of Pb Film Growth on Cu Surfaces***, **G.L. Kellogg**, R. Plass,* Sandia National Laboratories **INVITED**

To develop a more fundamental understanding of the microscopic processes that control the dynamics of liquid-metal wetting and spreading, we are using low energy electron microscopy (LEEM) to investigate the properties of Pb overlayers on Cu surfaces. The experiments probe a wide range of surface processes -- from the dynamic properties of submonolayer films to the growth, ripening and melting of three-dimensional islands. Measurements of changes in morphology during surface alloying and de-alloying provide new insights into the nature of submonolayer Pb structures on Cu(100). By combining different imaging modes of the LEEM, we have discovered an interesting correlation between the shape of three-dimensional Pb islands and the domain structure of the Pb/Cu(100) overlayer upon which they grow. Direct observations of Ostwald ripening combined with modeling studies indicate that mass transfer between three-dimensional islands is inhibited at domain boundaries of the submonolayer structure. The implication o f these and other results as they relate to liquid-metal flow processes will be discussed. Sandia National Laboratories is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the U. S. DOE under Contract DE-AC04-94AL85000.

3:40pm **SS3-MoA6 Comparison of Behavior of Wetting-related Adsorption Transitions in the Ga-Pb, Ga-Tl, Ga-Pb-Tl Systems***, **H. Shim**, P. Wynblatt,* Carnegie Mellon University*; D. Chatain,* CRMC2-CNRS, France

In this presentation, we summarize investigations of prewetting behavior in three Ga-rich liquid alloy systems, Ga-Pb, Ga-Tl and Ga-Pb-Tl. The adsorption of Pb and/or Tl at the surfaces of these alloys was determined by Auger electron spectroscopy, as a function of temperature and composition. Most of the surface composition measurements reported were performed below the freezing points of the alloys (~300 K) where the alloys exist in a supercooled liquid state. However, measurements cannot be conducted below about 240 K, where the alloys undergo non-equilibrium freezing (presumably by homogeneous nucleation). Extrapolation to lower temperatures of the results obtained in the meta-stable liquid state (between 300 and 240 K) indicates the existence of possible prewetting critical points at about 240 K for Ga-Pb alloys, and at about 150 K for Ga-Tl alloys. The motivation for studying Ga-Pb-Tl ternary alloys was that small additions of Tl might raise the prewetting critical point of Ga-Pb to temperatures above 240 K, and lead to more definitive observations of prewetting behavior. However, although ternary Tl additions do lead to increased Pb adsorption, as expected, the temperature of a possible prewetting critical point is lowered even further to about 215 K.

4:00pm **SS3-MoA7 Shape Relaxation of Crystals via Layer-by-Layer Pealing Observed in Real Time***, **K. Thürmer**, J.E. Reutt-Robey, E.D. Williams,* University of Maryland

How does a small faceted crystal adjust its shape to a changing temperature and is it possible to reach its equilibrium shape? A positive answer to the latter question would allow an elegant experimental determination of absolute values of surface and step free energies.@footnote 1@ Small defect-free crystals near equilibrium experience an energy barrier for both growth and removal of atomic layers on a facet. Under growth conditions the 2D nucleation barrier gives rise to shape oscillations.@footnote 2@ Recently Mullins et al.@footnote 3@ concluded that for crystals larger than a few nm the magnitude of this barrier prevents surface free energy driven reshaping. We studied µm sized Lead crystals with an variable temperature STM under UHV-conditions. By tracking several crystals during a temperature increase from 110°C up to 205°C we confirmed Mullins suggestion that these crystallites are immobilized in their initial shapes. To investigate how a crystal establishes its shape we quenched the sample to temperatures between 65 and 110°C. STM observations of the (111) top facet starting shortly after the quench reveal a scenario of facet growth, where all layers smaller than a critical size peal off one-by-one. Uwaha@footnote 4@ treated the kinetics of such a collapse of step loops applying a constant critical size. Our experiments indicate a modification of the critical radius by a slow redistribution of atoms over the curved region of the crystal. @FootnoteText@ Work supported by NSF-MRSEC @footnote 1@ H.P. Bonzel et al, to be published @footnote 2@ J. Tersoff et al, Phys Rev. Lett. 70, 1143 (1993) @footnote 3@ W.W. Mullins et al, J. Am. Ceram. Soc., 83, 214 (2000) @footnote 4@ M. Uwaha, J. Phys. Soc. Jap., 57, 1681 (1988).

4:20pm **SS3-MoA8 LEEM Study of Mass Transport on Si(111)***, **H. Hibino**, C.-W. Hu,* Arizona State University*; T. Ogino,* NTT Basic Research Laboratories, Japan*; I.S.T. Tsong,* Arizona State University

How does the surface morphology change during annealing, growth, and/or sublimation? In order to ask the question, we need understanding of the process of the mass transport. In this paper, we investigate two aspects of mass transport on Si(111) using LEEM. One aspect is the decay of 2-dimensional islands or holes near the phase transition between 1x1 and 7x7. The evolution of the island or hole provides the information about the rate-limiting process. The radii of the islands and holes show power-law dependences on time. The measured exponents are close to 1/3 rather than 1/2. This means that the decay is governed by the diffusion of atoms on the terraces rather than the attachment and detachment of atoms at the steps. We also measure the decay rate as a function of the temperature, and clarify that the decay rate changes steeply at the phase transition between 1x1 and 7x7. The decay rate is faster on 1x1 than on 7x7. The other aspect is the shape changes of the islands and holes during the 1x1-to-7x7 phase transition. The atom density in 1x1 is higher than that in 7x7. This difference in the atom density causes the steps to advance during the 1x1-to-7x7 phase transition. Comparing the changes of the islands and holes, the island tends to capture more atoms than the hole. More atoms are incorporated into the step from the lower terrace than the upper terrace. The 7x7 reconstruction nucleates at the upper step edges. Therefore, this result as well as the faster decay rates of islands and holes on 1x1 than on 7x7 suggest that the mass transport is faster on 1x1 than on 7x7.

4:40pm **SS3-MoA9 First-Principles Study of Vacancy Ionization Effects on Surface Diffusion***, **H.Y.H. Chan**, E.G. Seebauer,* University of Illinois, Urbana-Champaign

While the effects of charged point defects on diffusion in bulk semiconductors have been studied extensively for many years, such phenomena have received almost no attention in connection with diffusion on surfaces. Recent studies in our laboratory using second harmonic microscopy (SHM) on Si have strongly suggested that charged vacancies can significantly affect observed activation energies and prefactors in a manner analogous to that observed for bulk diffusion. Furthermore, these studies have revealed significant non-thermal effects of photon illumination that also appear to be mediated by charged vacancies. Unfortunately, a more quantitative and complete description of these various phenomena requires a knowledge of the energy levels of the various surface vacancy charge states. Until now these energy levels have remained unknown on Si. We report herein the results of density-functional-theory based quantum calculations that fill this gap. Total-energy calculations using a plane-wave/pseudopotential approach within the local-density approximation were used to determine the charge-state dependent formation energies of vacancies as a function of Fermi level. The computed electronic structure, lattice reconstruction, and their effects on surface diffusion are discussed.

5:00pm **SS3-MoA10 Surface Supercooling and Stability of Si(111)-"1x1" High Temperature Phase***, **C.-W. Hu**,* Arizona State University*; H. Hibino, T. Ogino,* NTT Basic Research Laboratories, Japan*; I.S.T. Tsong,* Arizona State University

Si(111) high temperature phase transition is one of the most studied surface processes. It is well known that high temperature "1x1" phase converts into the most stable (7x7) surface reconstruction at about 830°C by the first order phase transition. However, the high temperature "1x1" phase can be locked down to 10~20°C below the phase transition temperature. This supercooling behavior is in situ observed by low energy electron microscopy within µm-sized two-dimensional depressions on Si(111) surface. The phenomenon can be readily explained as the lack of the nucleus of (7x7) reconstruction in depressions because the step edges of upper terrace take the roles of nucleation centers for stable (7x7) reconstruction. The supercooling temperatures are observed strongly depending on the sizes of depressions and the cooling rates of Si substrate. A normal depression with (7x7) reconstruction on it is formed by fast cooling through phase transition temperature. In this way, the filling-up rates can be measured respectively for supercooling depressions and normal depressions. The preliminary experimental results exhibit the downward movement of Si adatoms from (7x7) upper terrace and the step-edge attachment within depressions are responsible for the stability of Si(111)-"1x1" supercooling phase.

Thin Films
Room 203 - Session TF-MoA

Atomic Layer Chemical Vapor Deposition II

Moderator: S.M. Rossnagel, IBM T.J. Watson Research Center

2:00pm **TF-MoA1 The Effect of Atomic Layer CVD Flow Parameters on the Growth Orientation of AlN Thin Films***, **J.N. Kidder**, J.W. Rogers, T.P. Pearsall,* University of Washington

We have observed a strong dependence of growth orientation on reactant pulse length in an atomic layer CVD of AlN. The AlN thin films were deposited on Al@sub2@O@sub3@ and Si substrates at 523-723 K and 25 Torr using an amine-alane Al source. The Al precursor, dimethylethylamine alane (DMEAA) and ammonia were delivered to the growth surface in separate steps. Strict self-limited adsorption did not occur for the DMEAA at these process conditions but a kinetic barrier to rapid decomposition of DMEAA coupled with process flow control provided a means to generate film formation through a sequence of adsorption/reaction steps. We observed that film microstructure was strongly dependent on ALCVD pulse lengths and substrate temperature. By this process, crystalline AlN films were deposited at temperatures as low as 573 K. AlN films deposited on Si(100), Si(111), Al@sub2@O@sub3@(00.1) tended to show a preferred orientation with the AlN{00.1} planes aligned parallel to the substrate surface. AlN{11.0}oriented growth was observed on Al@sub2@O@sub3@(01.2)substrates. The growth orientation was strongly dependent on the pulse length and substrate temperature. Both random and well-oriented films were deposited on Al@sub2@O@sub3@(00.1). By varying the reactant flow sequence the growth orientation on Al@sub2@O@sub3@(01.2) could be controlled to be either AlN{00.1} or AlN{11.0}oriented. X-ray four circle diffractometry scans showed in-plane orientations associated with epitaxial alignment for films deposited at temperatures as low as 673 K. These results illustrate the potential for using sequential reactant delivery in CVD to tailor the microstructure of thin film materials.

2:20pm **TF-MoA2 Atomic Layer Deposition (ALD) Films for Advanced Capacitors***, **O. Sneh**, R.C. Phelps, T. Seidel,* Genus, Inc.

We will present new data on Atomic Layer Deposition (ALD) films. Films were deposited on our recently announced dielectric ALD processing module. Our ALD process equipment, now at beta phase, is a single wafer 200 mm process module that operates and fully integrates with Genus Lynx2 cluster tool. Data pertain for as deposited, fully stoichiometric Al@sub 2@O@sub 3@ and Ta@sub 2@O@sub 5@ films that are continuous and amorphous in the useful range of 15-200 Å, will be presented. CV and IV measurements indicate leakage current in the 10@super -8@ A/cm@super 2@ range for these films in the useful thickness range and dielectric constants of ~7.5 (Al@sub 2@O@sub 3@) and ~25 (Ta@sub 2@O@sub 5@). Step coverage over >15:1 aspect ratio structures with 100 nm width is 100 %. Supporting data will be presented and discussed. We will review data for dielectric films on silicon as well as over CVD and ALD deposited metal nitride thin films. Some aspects and applications of MIM and SIS capacitor technology development will be reviewed.

2:40pm **TF-MoA3 Tungsten Atomic Layer Deposition: Nucleation and Growth on Oxide Surfaces***, **S.M. George**, J.W. Klaus, J.W. Elam, C.E. Nelson, R.K. Grubbs, S.J. Ferro,* University of Colorado **INVITED**

Tungsten atomic layer deposition (ALD) can be accomplished by separating the binary reaction WF@sub6@ + Si@sub2@H@sub6@ --> W + 2SiHF@sub3@ + 2H@sub2@ into two self-limiting half-reactions.@footnote 1@ The two self-limiting half-reactions are: (A) W-SiHF@sub2@* + WF@sub6@(g) --> W-WF@sub5@*+ SiHF@sub3@(g); and (B) WF@sub5@* + Si@sub2@H@sub6@(g) --> W-SiHF@sub2@* + 2H@sub2@(g) + SiHF@sub3@(g). In situ FTIR spectroscopy studies have determined the temperatures and pressures required for these two half-reactions to reach completion. In situ spectroscopic ellipsometry studies have examined the growth of W ALD films. Successive exposure to WF@sub6@ and Si@sub2@H@sub6@ in an ABAB... reaction sequence produced W ALD at a rate of 2.5 Å per AB cycle at 425 K. The nucleation and growth during W ALD on SiO@sub2@ and Al@sub2@O@sub3@ surfaces have also been studied using Auger electron spectroscopy (AES). The AES results displayed an initial nucleation period of several AB cycles. After the deposition of one tungsten monolayer, the AES signals for W and Si oscillated dramatically versus WF@sub6@ and Si@sub2@H@sub6@ exposures. These studies indicated that W ALD displays nearly ideal layer-by-layer (Frank van der Merwe) growth after the initial nucleation period. W ALD can be used together with Al@sub2@O@sub3@ ALD@footnote 2@ to fabricate W/Al@sub2@O@sub3@/W/Al@sub2@O@sub3@ nanolaminates. Cross-sectional transmission electron microscopy (TEM) studies have examined the W/Al@sub2@O@sub3@/W/Al@sub2@O@sub3@ nanolaminates deposited on Si(100). The growth of the nanolaminates is dependent on the details of the surface chemistry during the nucleation of W ALD on Al@sub2@O@sub3@. @FootnoteText@ @footnote 1@ J.W. Klaus, S.J. Ferro and S.M. George, Thin Solid Films 360, 145 (2000). @footnote 2@ A.W. Ott, J.W. Klaus, J.M. Johnson and S.M. George, Thin Solid Films 292, 135 (1997).

3:20pm **TF-MoA5 Radical Enhanced Atomic Layer Deposition (ALD) of Diffusion Barrier Films at Low Temperatures***, **A. Sherman**, F. Turner,* Sherman & Associates*; C. Pan,* ASM America*; S.M. Rossnagel,* IBM T.J. Watson Research Center **INVITED**

Atomic Layer Deposition (ALD) processes can be extended to low deposition temperatures by the use of an appropriate free radical in place of a conventional molecular reactant. Typically, the ALD process has been carried out using stable gaseous reactants, and the surface reaction was thermally driven in the temperature range of 300-400°C. Radical enhanced ALD has been carried out for the deposition of Ti, TiN, Ta, TaN, and Al@sub 2@O@sub 3@ at temperatures from room temperature to 400°C. Remote inductive plasma sources, operating at frequencies from 400 KHz to 13.56 MHz were used to generate free radicals from O@sub 2@, N@sub 2@, H@sub 2@ and NH@sub 3@ gas sources. Residual gases in the reactor chamber were removed after each dosing step by evacuating the chamber with a vacuum pump, rather than purging with an inert gas. Titanium films were deposited from 25-250°C using titanium tetrachloride and hydrogen. The conformality in high aspect ratio vias and the thickness uniformity across 200 mm wafers was excellent. Tantalum films were deposited using tantalum pentachloride and hydrogen at temperatures from 25-400°C. Additional experiments have been carried out using TDMAT (tetrakis(dimethylamido)titanium) at room temperature to deposit titanium bearing films. Aluminum oxide films were deposited at room temperature from TMA (trimethyl aluminum) and oxygen. Experimental results, including SEM observations in high aspect ratio features, as well as chemical analysis (RBS, XPS, AES) and structural (XRD) measurements will be reported.

4:00pm **TF-MoA7 Vacuum Beam Studies of Radical Enhanced Atomic Layer Chemical Vapor Deposition***, **F. Greer**, D. Fraser, J.W. Coburn, D.B. Graves,* University of California, Berkeley

As device dimensions continue to shrink and aspect ratios continue to increase, it will become increasingly difficult to deposit highly conformal thin films for applications such as Cu diffusion barrier layers. Atomic Layer Chemical Vapor Deposition (ALCVD) has been proposed as one way to achieve these highly conformal thin films due to the layer-by-layer growth that is possible when a precursor and a stable reactive specie are introduced sequentially into a deposition chamber. One problem with conventional ALCVD is that the deposition temperatures that are required to achieve reasonable growth rates can be relatively high, and may be incompatible with the integration of these barrier films with temperature-sensitive films such as organic low-k materials.@footnote 1@ It has been recently proposed that by using a more reactive specie like a radical as the second reactant, atomic layer film deposition at lower temperatures may be possible.@footnote 2@ It may also be possible to find radical surface treatments that either promote or hinder adsorption of the precursor specie on different surfaces, allowing even more control over the deposition process. This work focuses on the tetrakisdiethylamide class of precursors for the deposition of nitrides and other films. By directing independent beams of these precursors and hydrogen radicals at different surfaces (inc. Si, SiO@sub 2@, and Au), deposition parameters of interest such as the sticking and reaction probabilities of these compounds have been measured as a function of temperature and surface preparation. The products evolved from the surface during each step of the deposition process, including the precursor ligands and surface reaction products, have also been measured using modulated beam mass spectrometry as a function of these same parameters. XPS analysis of the deposited films will also be presented. @FootnoteText@ @footnote 1@A. Satta et al. Spring MRS Meeting 2000 D6.5 @footnote 2@A. Sherman US Patent 5916365.

Biomaterial Interfaces
Room 202 - Session BI-TuM
Protein-Surface Interactions

Moderator: B.D. Ratner, University of Washington

8:20am **BI-TuM1 Quantitative Analysis of Protein Adsorption Kinetics*, V. Hlady,*** University of Utah **INVITED**

Protein adsorption from aqueous solution is determined by a "match" between two interfaces, one between the protein and the aqueous solution and the other between the adsorbent surface and the solution. A subtle interplay between polar and non-polar interactions regulates protein stability and plays a decisive role in protein interactions with the adsorbent surface. Other factors include the adsorbent's surface energetics, charge, rugosity, and the structure of water at both interfaces, i.e. their respective hydrophilicity and interfacial hydration layers. In order to characterize and predict protein adsorption, one seeks information about adsorption isotherms and kinetics, conformation of adsorbed proteins, number and character of surface-bound protein segments, and the physical parameters describing the adsorbed protein layer. The most powerful techniques for protein adsorption studies include optical and spectroscopic methods. These methods can provide insight into protein concentration, conformation and dynamics at interfaces. We have designed a spatially-resolved total internal reflection fluorescence spectroscopy method (1-D TIRF) to measure competitive adsorption kinetics of human plasma proteins. When combined with autoradiography and surface hydrophobicity gradients, 1-D TIRF experiments provide a quantitative description of protein adsorption and desorption kinetics as a function of surface hydrophobicity. As an example we will show the analysis of the adsorption kinetics from a binary solution mixture of human serum albumin (HSA) and human low density lipoproteins (LDL) onto the model surface with a density gradient of octadecyldimethylsilyl chains on fused silica (C18-silica gradient). The adsorption and desorption rate constants are obtained by fitting the experimental results to an adsorption model that accounts for the mass transport effects and the surface density of the C18 groups.

9:00am **BI-TuM3 Investigation of the Structure and Dynamic of Proteins on Surfaces by EPR Spectroscopy: Annexin XII as an Exploratory Example*, T. Risse,*** *W.L. Hubbell,* University of California, Los Angeles*; M. Isas, H. Haigler,* University of California, Irvine

Site-directed spin labeling (SDSL) has become an important tool for the investigation of structure and dynamics in proteins. The SDSL strategy involves introduction of one or two nitroxide side chains (R1) at selected positions in the protein sequence, followed by analysis of the electron paramagnetic resonance (EPR) spectrum in terms of secondary and tertiary structure. To increase the information content of the SDSL experiment, and to examine protein structure and dynamics at interfaces, oriented arrays of spin-labeled proteins on surfaces are now under investigation. Initial experiments have employed the helical protein Annexin XII adsorbed to single lipid bilayers supported on glass or mica surfaces. For molecules oriented in 2-dimensions, the tensorial nature of the Hamilton operator gives rise to angular dependent EPR spectra which can be used to extract the orientation of the nitroxide relative to the surface. Such information is of paramount importance for determining the topography of proteins bound to surfaces. In addition, direct information on the structure and interactions of the protein at the surface is obtained from the dynamics of the side chains inferred from the spectral lineshape. Results for R1 residues at sites 213, 147, 148 and 154, 156 in oriented monolayers of Annexin XII will be discussed relative to these points.

9:20am **BI-TuM4 A Surface Plasmon Resonance Biosensor Study of Protein Interactions with Thin Apatite Films*, H.B. Lu,*** University of Washington*; B.J. Tarasevich,* Battelle Pacific Northwest National Laboratory*; C.T. Campbell, C. Giachelli, B.D. Ratner,* University of Washington

The primary objective of this research is to study protein interaction with a well-characterized apatite film using a surface plasmon resonance (SPR) sensor. Due to the remarkable osteointegration properties of apatite as an implant material, protein adsorption onto this type of material has been intensively studied. It is believed that knowledge on protein adsorption to such apatite surface will help us to understand the body's response to foreign materials and improve implant performances. However, due to the limitations of analytical tools for either material characterization or protein adsorption, few useful conclusions have been reached. In this study, a gold SPR sensor has been functionalized with a carboxylic acid-terminated self-assembled monolayer and then coated with an apatite thin film grown with the surface-induced mineralization technique. The apatite mineral films have been well characterized using surface analytical tools including TOF-SIMS, XPS, FTIR, and AFM, as well as bulk analytical technique XRD. SPR is an optical phenomenon that is very sensitive to refractive index changes perturbing the evanescent wave at metal-liquid interfaces. By coating the SPR sensor with a thin apatite film, we took advantages of continuous and label-free monitoring, and thus studied protein interactions with apatite in real time. The proteins studied include phosphorylated Rat His osteopontin (p-OPN), non-phosphorylated Rat His osteopontin (n-OPN), and bovine serum albumin (BSA). The p-OPN displayed very distinguishable adsorption/desorption behavior from that of n-OPN and BSA. The p-OPN has a higher affinity toward the apatite surface, compared to n-OPN and BSA. The p-OPN may have inhibited mineral growth upon adsorption, while BSA may have promoted slight mineral growth upon adsorption. On the other hand, these proteins behaved non-selectively when adsorbing onto control surfaces including bare gold, a COOH-terminated SAM and an NH2-terminated SAM.

9:40am **BI-TuM5 Protein Adsorption to Plasma Functionalized Surfaces Using Surface Plasmon Resonance Spectroscopy and Atomic Force Microscopy*, M.T. van Os,*** University of Twente*; A.T.A. Jenkins,* Max Planck Inst. for Polymer Res.*; M. Péter,* University of Twente*; R. Förch,* Max Planck Inst. for Polymer Res.*; R.B. Timmons,* The Univ. of Texas at Arlington*; W. Knoll,* Max Planck Inst. for Polymer Res., Germany*; G.J. Vancso,* University of Twente, The Netherlands

Plasma modification provides a powerful tool to tailor the surface properties of materials. Surface characteristics such as wettability, chemistry and morphology are known to influence protein adsorption, and the subsequent attachment and spreading of cells on biomaterials. To improve the understanding of protein-surface interactions we functionalized gold and silicon surfaces with amino or ether groups, using radio frequency plasma polymerization of ethylenediamine, allylamine, cycloheptylamine and di(ethyleneglycol)vinylether (EO2V). The functional group density at the surface was controlled by using different monomers or by variation of the input power during the plasma deposition. The adsorption of the proteins fibrinogen, bovine serum albumin and immunoglobulin G to these surfaces was measured in situ with surface plasmon resonace spectroscopy. The tenacity of the protein adsorption on the different substrates was also measured, after removing elutable protein with 1% sodium dodecyl sulfate (SDS) solution. After drying, the protein layers were studied by tapping mode atomic force microscopy (TM-AFM). The results obtained show that both the protein adsorption to and the retention on the surfaces are affected greatly by the surface functionalities. All the amine functionalized surfaces showed a high affinity toward the proteins, and thin dense layers of adsorbed protein remained on these surfaces, even after rinsing with SDS solution. A large contrast in protein affinity was observed between the EO2V films polymerized at different power input conditions. A dramatic reduction in both initial adsorption and retention of all proteins was observed on these films with decreasing power. The low degree of cross-linking, as well as the high retention of ether content during the polymerization of EO2V under low power input conditions is thought to result in the production of biologically non-fouling surfaces.

10:00am **BI-TuM6 How to Make and Analyze Cross-linked Monolayers of Mytilus Edulis Foot Proteins (Mefp)*, H. Elwing,*** *K. Mjorn,* Lab of Interface Biophysics, Sweden*; K. Uvdal, M. Fahlman,* Linkoping University, Sweden*; J Lausmaa,* National Testing and Res. Institute, Sweden*; F. Hook,* Lab of Interface Biophysics, Sweden

The Mefp proteins are potential candidates as "tissue glues" in biomaterial applications. Several of the Mepf proteins contain high amounts of DOPA (dihydroxyphenylalanin). On oxidation to o-quinone the DOPA molecules become highly reactive and forms a base for cross-linking of the proteins in the byssus threads as well as binding to solid surfaces. We have developed an experimental model consisting of polar siliconoxide surfaces and apolar alkanethiol surfaces. On this surfaces we follow adsorption of purified Mefp-1 with the use of optical methods such as surface plasmon resonance (SPR) and high precision ellipsometry. Periodate induced crosslinking of the molecular layers is then followed by Quarts crystal microbalance (QCM-D) and ellipsometry. At apolar surfaces we found a reduction of layer thickness from about 20 nm to about 4 nm as well as a significant reduction of the viscoelastic properties of the protein layers as measured by QCM-D. On the other hand, adsorption of Mefp-1 on polar surfaces resulted in a protein layer that was thin and dense from the beginning and cross-linking resulted only in significant small change of layer thickness and viscoelasticity of the mefp-1 layer. It was obvious that adsorption of Mefp-1 to polar surfaces significantly reduced the possibility of cross-linking most probably due to binding engagement of the DOPA side chains to the silicon oxide surface. We also made an analysis with photoelectron spectroscopy (XPS). High-resolution spectra at normal and glancing take off angles were obtained with a particular emphasis placed on the C 1s core level. Four distinct peaks were visible in the non-deconvoluted spectrum. Carbon-nitrogen and carbon-oxygen bonds were studied as a function of depth, crosslinking and the polarity of the substrate. Significant differences were found and is now subjected to a more detailed analysis together with data from time of flight secondary ion spectroscopy (TOF-SIMS).

10:20am **BI-TuM7 Assessment of Fibronectin Conformation Adsorbed to Polytetrafluoroethylene Surfaces from Serum Protein Mixtures and Correlation to Support of Cell Attachment in Culture***, **D.W. Grainger**,* Colorado State University*; G. Pavon-Djavid, V. Migonney, M. Josefowicz,* Universite Paris, France

Fluoropolymer surfaces in biotechnology applications are notorious for tightly adsorbing proteins that do not support cell attachment. Reasons for this remain confusing but surround both the population and conformation of proteins adsorbed competitively from physiological milieu that do not interact with cell adhesion receptors. In this study, polytetrafluoroethylene (PTFE) surfaces were exposed to buffered aqueous solutions containing radio labeled (@super 125@I) human fibronectin (Fn), fibronectin:serum albumin (BSA) binary mixtures of various ratios, or whole human plasma dilutions (one hour). Total adsorbed fibronectin and albumin following rinsing were quantified on PTFE. @super 125@I-labeled monoclonal antibodies against either the fibronectin cell adhesion (containing the RGDS integrin recognition motif) or the fibronectin amino terminal domains were used to probe accessibility of each of these fibronectin regions post-adsorption. Human umbilical vein endothelial cells (HUVECs) were then cultured on PTFE surfaces pre-exposed to each of these protein adsorption conditions and compared to identical conditions on tissue culture polystyrene (TCPS) controls. Fibronectin adsorption to PTFE is dependent upon the concentration of albumin co-adsorbing from solution: albumin out-competes fibronectin for PTFE surface sites even at elevated nonphysiological Fn:HSA ratios. Antibodies against Fn do not readily recognize Fn adsorbed on PTFE as the HSA co-adsorption concentration in either binary mixtures or in plasma increases, indicating albumin masking of adsorbed Fn. At higher Fn:HSA ratios, albumin co-adsorption actually improves anti-Fn antibody recognition of adsorbed Fn. HUVEC attachment efficiency to PTFE after protein adsorption correlates with amounts of Fn adsorbed and levels of anti-Fn antibody recognition of Fn on PTFE, linking cell attachment to integrin recognition of adsorbed Fn density and Fn adsorbed conformation on PTFE surfaces.

10:40am **BI-TuM8 Protein Adsorption on Self-assembled Polyelectrolyte Multilayer Films***, G.D. Ladam,* Institut Charles Sadron, France*; F.J.G. Cuisinier,* Federation de Recherche "Odontologie", France*; G. Decher,* Institut Charles Sadron, France*; J. Voegel,* Federation de Recherche "Odontologie", France*; **P. Schaaf**,* Institut Charles Sadron, France

Alternating polyelectrolyte films were constructed by the sequential adsorption of poly(allylamine hydrochloride) (PAH) and polystyrenesulfonate (PSS) onto a silica surface. The film build-up and the further adsorption of proteins (human serum albumin (HSA), ribonuclease A, lysozyme, alpha-lactalbumine, myoglobine) were followed in situ versus time by means of scanning angle reflectometry. We investigated first the influence of the isoelectric point of the proteins on their adsorption onto positive (PAH ending) and negative (PSS ending) multilayers. At a protein concentration of 0.25mg/ml at pH 7.4 and in the presence of Tris HCl 10-2M, 0.15M NaCl buffer, all proteins adsorbed on both positive and negative polyelectrolyte films with thicknesses varying from the monolayer or less, up to thicknesses equivalent to at least 4 protein layers. Thick protein layers were observed when proteins and films were oppositely charged. The adsorption of HAS onto both films was investigated as a function of the protein concentration and the NaCl concentration of the adsorbing solution. It was found that on PSS ending multilayers exhibiting a similar charge as albumin, the proteins still adsorb but only a monolayer can be reached. On the other hand, on PAH ending multilayers thick protein films are observed. The adsorbed amount depends also critically on the NaCl concentration of the adsorbing solution. Desorption experiments were also performed and depending on the salt concentration of the rinsing solution one can observe no desorption or partial desorption (up to 50% of the adsorbed amount). A microsocopic model will be discussed trying to explain these experimental findings.

11:00am **BI-TuM9 Desorption/Ionization Mass Spectrometry on Porous Silicon Surfaces***, **Z. Shen**, J.E. Crowell,* University of California, San Diego*; G. Siuzdak,* The Scripps Research Institute

A new desorption/ionization strategy for biomolecular mass spectrometry has been developed based on pulsed laser desorption/ionization from a porous silicon surface. Desorption/ionization on silicon (DIOS) uses porous silicon to trap analytes deposited on the surface and laser radiation to vaporize and ionize these molecules. DIOS is demonstrated for a wide range of small molecules as well as biomolecules at the femtomole and attomole level with little or no fragmentation, in contrast to what is typically observed with other direct desorption/ionization approaches. Porous silicon surfaces were prepared using electrochemical etching. While DIOS has been universally applicable for a range of mass analyses, its success is highly dependent upon the preparation of the sample and the nature of the porous silicon surface. Different etching parameters, including silicon wafer crystal orientation, dopant type, dopant level, light intensity, current density, etching solution, and etching time were studied to optimize DIOS-MS performance. Scanning Electron Microscopy (SEM) was used to examine the pore structure and correlate it with DIOS-MS performance. We will also demonstrate the application of DIOS-MS to small molecule analysis and quantitation, protein identification, on-chip reaction monitoring, on-chip separation and post-source decay structure analysis. DIOS offers many unique advantages including good sensitivity, low background ion interference, and high salt tolerance. Desorption/ionization on porous silicon (DIOS) permits analysis of a wide range of molecules with very good sensitivity and a demonstrated potential for automation, as well as compatibility with microfluidics and microchip technology on silicon.

11:20am **BI-TuM10 Determination of Surface-Protein Equilibrium Binding Constants by MALDI Mass Spectrometry***, **G.R. Kinsel**, J. Zhang, R.B. Timmons, H. Qiu,* University of Texas at Arlington

We have recently demonstrated that matrix assisted laser desorption / ionization (MALDI) mass spectrometry offers a new approach for the characterization of surface-protein interactions. Our work demonstrates that strongly surface-retained proteins are poorly incorporated into the MALDI matrix crystals, leading to inefficient ionization of these species. In effect, the surface-deposited protein MALDI ion signal approaches zero as the quantity of deposited protein approaches the quantity strongly retained by the surface. Furthermore, as expected, the protein MALDI ion signals exhibit Langmuir type behavior as the surface concentration of the protein is reduced, i.e. the protein MALDI ion signal versus surface concentration response becomes asymptotic at low protein surface concentrations. Analysis of the protein MALDI ion signal versus surface concentration data allows the equilibrium surface-protein binding constant to be established. In our current work this approach to the determination of surface-protein binding constants has been applied to a number of smaller peptides and proteins deposited on a variety of polymeric biomaterials. Expected trends are observed, particularly with regard to the influence of electrostatic interactions between acidic or basic surfaces and basic or acidic proteins in solution. In addition, we have used the MALDI approach to examine the elutability of surface-bound proteins as a function of solvent choice. Our studies indicate that protein solubilization as a function of solvent choice is strongly influenced by the chemistry of the surface-protein interaction.

11:40am **BI-TuM11 The Molecular Orientation Distribution of an Electrochemically Active Protein Monolayer Adsorbed to Indium-Tin Oxide***, S. Saavedra, **R.T. Robertson**, S.B. Mendes, N.R. Armstrong,* University of Arizona

The relationship between molecular orientation and heterogeneous electron transfer behavior in immobilized films of redox-active proteins is being investigated using absorbance and fluorescence techniques that combine the information content of spectroele ctrochemistry with the sensitivity of the single-mode, planar waveguide geometry. Spectroelectrochemistry of surface confined, redox-active films can be performed with a pathlength enhancement of approximately 4,000 relative to a transmission geometry. T he use of this approach to determine the tilt angle distribution of the porphyrin molecular planes in a submonolayer of electrochemically active cytochrome c adsorbed to an indium-tin oxide electrode will be described. Developing a better understanding of the relationship between protein film structure and redox activity may aid efforts to rationally design protein-based molecular devices in which control of vectorial electron transfer is a prerequisite for efficient operation.

Electronics
Room 312 - Session EL+NS-TuM
Molecular Electronics

Moderator: Y. Liang, Pacific Northwest National Laboratory

8:20am **EL+NS-TuM1 Molecules, Hierarchical Assembly and Architecture of Moletronic Computers***, **W.L. Warren**,* Defense Advanced Research Projects Agency **INVITED**

While the rapid miniaturization of electronics has driven much of the development of computation and information systems, it is anticipated that future computational demands for performing calculations orders of magnitude faster with less power. To create discovery beyond silicon, the DARPA Moletronics program is proposing that both computational functionality and input/output architecture can be designed in molecular systems. These systems will high device density (scaleable to 10@super 12@ device/cm@super 2@) and be amenable to greatly simplified manufacturing fabrication using hierarchical-assembly. It is anticipated that architecture, a top-down approach will play an immense role in steering discovery. Moletronics is focussed on developing technologies based on the self-assembly of molecular components to act as devices, switches, and interconnects. The program does not clone contemporary electronic devices with molecular scale components, but rather create functionality that exploits what molecules are good at (self-assembly, thermodynamic equilibrium, and charge storage media.) The trick for molecular computers will be to cope with defects and to realize hierarchical processes to manufacture the hardware. Hierarchical assembly is envisaged as a set of processes that will first assemble individual devices, then create functional blocks (circuits) from those devices and finally assemble systems from the blocks. It is a bottom-up manufacturing process whereas current microelectronics fabrication is based on top-down manufacturing using lithography. The talk will discuss three over-riding themes of the Moletronics program: (1) molecular devices, (2) hierarchical assembly, and (3) architecture including defect tolerance and algorithm development to find the defects. @FootnoteText@ @footnote 1@ The contributions of the contractors of the DARPA Moletronics program and fellow program managers, Bruce Gnade, Christie Marrian, and John Pazik are gratefully acknowledged.

9:00am **EL+NS-TuM3 Molecular Wires, Switches and Memories***, **J. Chen**,* Yale University **INVITED**

Molecular electronics has recently attracted much attention because of its potential application in future computational systems. Molecular wires and related strategically engineered structures (e. g., molecular switches and memories) offer an increased versatility in device design with reduced elements. Nanoscale molecular devices utilizing active self-assembled monolayer (SAM) as the active component will be reported. We will present results on: (1). measurements of through-bond conductance of symmetric metal/conjugated SAM/metal junctions where non-Ohmic thermionic emission was observed to be the dominant process, with isocyanide-Pd contacts showing the lowest thermionic barrier of 0.22 eV; (2). first realization of robust and large reversible switching behavior in an electronic device that utilizes molecules containing a nitroamine redox center (2'-amino-4,4'-di(ethynylphenyl)--5'-nitro-1-benzenethiolate) exhibiting negative differential resistance (NDR) and an on-off peak-to-valley ratio (PVR) exceeding 1000:1; while molecules containing a nitro-only redox center (4,4'-di(ethynylphenyl)-2'-nitro-1-benzenethiolate) exhibiting room temperature NDR; (3) demonstration of a two-terminal electronically programmable and erasable molecular memory cell with bit retention time greater than 10 minutes.

9:40am **EL+NS-TuM5 Dissimilar Metal Electrodes with Nanometer Interelectrode Distance: Fabrication and Application to Characterizing Self-Assembled Molecular Electronic Devices***, **M.A. Guillorn**, I. Lee,* University of Tennessee*; D.W. Carr, R. Tiberio,* Cornell Nanofabrication Facility*; E. Greenbaum, J. Lee,* Oak Ridge National Laboratory*; M.L. Simpson,* Oak Ridge National Laboratory and The University of Tennessee

In order to advance the state of molecular-scale electronics research, electrode structures capable of realizing metal/molecular monolayer/metal heterojunctions have been fabricated using a variety of novel techniques that allow direct electrical contact with single molecules and small groups of molecules. By using Au as the electrode material, thiol-based self-assembly techniques have been successfully applied to deposit organic-synthetic molecules between these electrodes, thereby permitting their electrical characterization. This is possible due to the symmetry of these molecules. Unfortunately these techniques do not lend themselves to measuring the electrical properties of asymmetric molecules. An example of this type of molecule is the Photosystem I (PSI) reaction center which is of demonstrated interest to molecular-scale electronics research. Self-assembly techniques have been developed to preferentially orient the PSI with respect to a Au substrate, however, the polar nature of this molecule inhibits the use of this technique for the formation of Au/PSI/Au heterostructures. In this paper we will discuss a flexible and reproducible process for fabricating dissimilar metal electrodes with nanometer interelectrode distance (DiMEND) using high-resolution electron beam lithography and liftoff pattern transfer. This process is capable of realizing electrode pairs with a minimum interelectrode distance of less than 6 nm. This technique provides a reproducible method for creating lateral structures well suited for the electrical characterization of asymmetric molecules for molecular-scale electronics applications. Applications of this technology to characterizing self-assembled molecular electronic devices will be presented.

10:00am **EL+NS-TuM6 Characterization of Gold/Pentacene and Pentacene/Gold Interfaces***, Q.T. Le, S. Zorba, E.F. Forsythe, L. Yan, **N.J. Watkins**, Y. Gao,* University of Rochester*; S.F. Nelson,* Colby College*; C.S. Kuo, T.N. Jackson,* The Pennsylvania State University

Among the conjugated oligomers used as active materials in the fabrication of organic thin-film transistors (OTFT), pentacene is one of the most promising materials due to its high field-effect mobility. The performance of pentacene based OTFTs is now comparable to that obtained from hydrogenated amorphous silicon TFTs. The interface formed between the organic semiconductor and the conducting layer strongly influences the current-voltage characteristics of OTFTs. We report the interface formation between gold (Au) and pentacene using x-ray and ultraviolet photoelectron spectroscopy (XPS and UPS). The morphology of the pentacene film deposited on the substrate was measured using atomic force microscopy, showing a pentacene layer with small grain size. XPS results indicate that Au does not chemically react with pentacene if Au is deposited onto pentacene or if pentacene is deposited onto Au. For Au deposited on pentacene the UPS results show that there is an initial binding energy shift of both the highest occupied molecular orbital of pentacene and the vacuum level attributed to the formation of a common fermi level for the Au and pentacene as the Au is deposited. The initial increase is then followed by a decrease in binding energy shifts that is attributed to a reduction of the polarization energy caused by the formation of a Au overlayer on the surface of the pentacene. For pentacene deposited onto Au the UPS results show that there is only a shift of the vacuum level to lower binding energy.shift of the vacuum level to lower binding energy.

10:20am **EL+NS-TuM7 Current-Induced Organic Molecule-Silicon Bond Breaking: Consequences for Molecular Devices***, **S.N. Patitsas**, G.P. Lopinski, O. Hul'ko, D.J. Moffatt,* National Research Council of Canada*; R.A. Wolkow,* National Research Council of Canada, Canada

The current carrying capacity of individual organic molecules covalently bound to silicon has been studied. Adsorbates comprised exclusively of saturated C-C bonds were found to be entirely stable whereas adsorbates containing pi-bonds could be controllably dislodged under modest conditions. The pi-bonds act as a chromophore, taking energy from a scattered electron, energy that can be selectively channeled into Si-C bond breaking. The class of adsorbates that are dislodged is closely related to unsaturated molecules widely investigated for enhanced molecular wire character. It is predicted that molecular devices containing such molecules will fail when operated. Measures to avoid current-induced bond breaking are described. New processes based upon the controlled bond breaking phenomenon are suggested.

10:40am **EL+NS-TuM8 Molecular Arrays and Individual Dopants Studied by Ultrahigh Vacuum Scanning Tunneling Microscopy***, **L. Liu**, J. Yu, N. Viernes, M.C. Hersam, N.P. Guisinger, J.W. Lyding,* University of Illinois

One aspect of molecular electronics is the fabrication of atomically precise molecular arrays on silicon substrates. Feedback controlled lithography (FCL) is used in conjunction with UHV STM to create atomically precise templates for molecular adsorption. Cobalt phthalocyanine (CoPc) molecules have been sublimed onto these templates and subsequently imaged in the STM. The difference between filled state and empty state images is explained. Current imaging tunneling spectroscopy (CITS) of CoPc is also performed and discussed. CoPc Molecular symmetry as well as the feature associated with the central Co atom are studied in all STM images. CITS has also been used to identify and study individual dopants on or near Si(100)2X1:H surfaces. For high quality UHV H-passivated Si(100) the Fermi level is unpinned at the surface, thus enabling the observation of subtle features including subsurface dopants. For example, boron atoms appear as slight hillocks in filled state images and as centro-symmetric depressions in empty states. Full CITS data sets and their analysis and interpretation will be presented. The same techniques will be used to present results for isolated Si dangling bonds created by FCL.

11:00am **EL+NS-TuM9 Direct Measurements of Electrical Transport through DNA Molecules***, **D. Porath**,* Tel Aviv University, Israel & Delft Univ. of Tech., The Netherlands, Israel*; A. Bezryadin,* Harvard University*; S. de Vries, C. Dekker,* Delft University of Technology, The Netherlands **INVITED**

Is DNA a conductor for electrical charges? This question has been heavily debated over the past few years, spurred by optical experiments that measured fluorescence quenching for DNA molecules and recent electrical measurements. Here we present measurements of electrical transport through short and well-defined DNA molecules that show large-gap semiconducting behavior. A 10.4 nm long, double-stranded poly(G)-poly(C) DNA molecule is connected to two metal nanoelectrodes that are separated by 8 nm. Nonlinear current-voltage curves with a voltage gap at low bias are observed at ambient conditions as well as in vacuum and at cryogenic temperatures. The voltage dependence of the differential conductance exhibits a peak structure, suggesting that transport of charge carriers is mediated by the molecular energy bands of DNA. Recent STM measurement on similar DNA molecules will be shown as well.

11:40am **EL+NS-TuM11 Whole-Cell Bio-computing in a Microelectronic Format***, **M.L. Simpson**,* Oak Ridge National Laboratory and The University of Tennessee*; G.S. Sayler, J. Fleming, B. Applegate, S. Ripp, D. Nivens,* University of Tennessee Center for Environmental Biotechnology

Even simple cells perform tremendously complex information processing operations involving memory (genes), sensing and feedback (promoters, regulatory proteins), and in some cases, interconnectivity (quorum sensing). For example, Escherichia coli, with a 4.6 million base-pair chromosome, has the equivalent of a 9.2-megabit memory to code for as many as 4,300 different polypeptides under the inducible control of perhaps several hundred different promoters. Yet, all of this functionality is contained in an area of approximately 1 square micron. Conversely, current predictions of the future of silicon integrated circuits indicate that 1 square micron of silicon will contain only a 245 bit memory or 1.66 simple logic gates by 2014. Obviously, silicon technology will not approach bacterial-scale integration within the foreseeable future. Furthermore, microorganisms have some qualities that are quite desirable for information processing devices and systems. Bacterial cells are relatively rugged "devices" that subsist in even extreme environments. Also, they are fairly easy to manipulate genetically, and have a diverse set of gene regulation systems. Furthermore, cells easily can be incorporated into a 3-dimensional structure instead of the planar structure of integrated circuits. And finally, cells self-assemble and self-replicate, and therefore are easy to manufacture. We will present our work to incorporate the information processing capabilities of living cells into a microelectronic format. This will include our work on the bioluminescent bioreporter integrated circuit (BBIC) for sensing applications, as well as our recent work to engineer more complex information processing and communication functions into whole cells deployed on integrated circuits.

Flat Panel Displays
Room 313 - Session FP-TuM
Luminescent Materials

Moderator: B.E. Gnade, University of North Texas

8:20am **FP-TuM1 Cross-sectional TEM Investigation of the Dead Layer of ZnS:Ag,Al Phosphors in Field Emission Displays***, **K. Kajiwara**,* Sony Corporation, Japan

The dead surface layer of blue-emitting ZnS:Ag,Al phosphor was investigated by means of cross-sectional transmission electron microscopy for the first time. It was found that the electron radiation-induced damage at 6 keV excitation gives rise to (i) the decomposition of ZnS and the evolution of sulfur at the topmost surface, and (ii) the nucleation and multiplication of lattice defects, for example vacancy clusters and dislocations, at the electron penetration layer of approximately 300 nm. It was estimated that the decompositon rate of ZnS and the nucleation rate of defects depend on the crystallinity and surface roughness of the ZnS host crystal. Based on these evidences, necessary specifications of ZnS:Ag,Al phosphor for the long lifetime of field emission display are to be discussed in this preliminary work.

8:40am **FP-TuM2 Enhanced Activator Interactions During Low Electron Energy Cathodoluminescence***, **C.H. Seager**, D.R. Tallant,* Sandia National Laboratories **INVITED**

We have measured the time decay of spectrally-resolved, pulsed cathodoluminescence (CL) and photoluminescence (PL) in several phosphors activated by rare earth and transition metal impurities; These included Y@sub 2@O@sub 3@:Eu, Y@sub 2@SiO@sub 5@:Tb, and Zn@sub 2@SiO@sub 4@:Mn; typical activator concentrations ranged from ~ 0.25 to 10%. The CL decay curves are always non-linear on a log-linear plot - i.e. they deviate from first order decay kinetics. These deviations are always more pronounced at short times and larger activator concentrations and are largest at low beam energies where the decay rates are noticeably faster. PL decay is always slower than that seen for CL, but these differences disappear after most of the excited species have decayed. We have also measured the dependence of steady state CL efficiency on beam energy. We find that larger activator concentrations accelerate the drop in CL efficiency seen at low beam energies. These effects are largest for the activators which interact more strongly with the host lattice. While activator-activator interactions are known to limit PL and CL efficiency in most phosphors, the present data suggest that a more insidious version of this mechanism is partly responsible for poor CL efficiency at low beam energies. This "enhanced" concentration quenching is due to the interaction of nearby excited activators;these interactions can lead to non-radiative activator decay, hence lower steady state CL efficiency. Excited state "clustering" appears to enhance these interactions, and this may be caused by the large energy loss rate of low energy primary electrons. In support of this idea, we find that PL decays obtained at high laser pulse energies replicate the non-linear decays seen in the CL data. This work was supported by DARPA. Sandia National Laboratories is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under contract #DE-AC04-94AL85000.

9:20am **FP-TuM4 Growth and Characterization of Pulsed Laser Deposited Zn2GeO4:Mn Green Thin Film Phosphors***, **T. Feng**, P.H. Holloway, D. Kumar, M. Davidson,* University of Florida*; J.M. Fitz-Gerald, H. Kim,* Naval Research Laboratory*; D.P. Norton, Y.E. Lee,* Oak Ridge National Laboratory

Pulsed laser deposition of Zn2GeO4:Mn oxide thin films on glass/ITO/ATO and Al2O3/Au/PZT substrates, which are potentially used for electroluminescent displays, has been investigated. A stoichiometric target Zn2GeO4:Mn was obtained by sintering a mixture of ZnO, GeO2 and MnO2 powder in air at 1020oC for 24 hrs. A green photoluminescence peak was obtained from the target at a wavelength of 540nm. Films were pulsed laser deposited on glass/ITO/ATO and Al2O3/Au/PZT substrate at an O2 pressure of 150~200 mTorr and a laser density of 0.8~1.6J/cm2. All deposited films were Zn-deficient in contrast to the stoichiometric target ratio for Zn/Ge of 2. The films deposited at 250oC on glass/ITO/ATO showed a Zn/Ge ratio of 1.02, while films deposited at 800oC were more Zn-deficient with a ratio of 0.82. The Zn2GeO4:Mn films deposited at 250oC on glass/ITO/ATO were amorphous, but recrystallized upon rapid thermal annealing at 800oC in Ar for 1 min. Photoluminescence with an intensity of 46 cd/m2 at a peak wavelength of 536nm was obtained from a 300nm film deposited on Al2O3/Au/PZT at 250oC followed by post-annealing at 750oC in air for 1 hr. Photoluminescence of 11 cd/m2 was obtained from a film deposited on glass/ITO/ATO followed by rapid thermal annealing at 800oC in Ar for 1 min. A surface particulate density of 2.42x105/cm2 was observed in the film deposited on glass/ITO/ATO substrate at a temperature of 250oC, O2 ambient pressure of 200 mTorr and laser density of 0.8mJ/cm2. Films deposited at 800oC showed a large density of pinholes, in addition to surface particulates. Annealing in O2 ambient resulted in a better PL intensity compared to annealing in air or Ar ambient.

9:40am **FP-TuM5 Energy Loss Mechanisms in Pulsed Laser Coated Cathodoluminescent Phosphors***, **W.J. Thomes**, P.H. Holloway,* University of Florida*; C.H. Seager, D.R. Tallant,* Sandia National Laboratories

Coatings of MgO and Al@sub 2@O@sub 3@ were pulsed laser deposited onto sedimented screens of Y@sub2@O@sub 3@:Eu and Y@sub 2@SiO@sub 5@:Tb to study energy loss mechanisms in the coatings and to predict their impact on cathodoluminescence (CL). The thickness of the pulsed laser deposited coatings, characterized by ellipsometry, TEM and AES sputter profiles, were varied from 75 to 500 Angstroms by changing the deposition time and oxygen background pressure. A Si shadow mask covered half of the sedimented powder during deposition to allow comparison of coated and uncoated powder. DC and pulsed cathodoluminescence data were collected using an Ocean Optics fiber optic spectrometer or a modified Kimball Physics electron gun, respectively. Light was collected using fiber optics connected to a photomultiplier tube or a CCD detector. The beam energies were varied from 0.8 to 4 keV, while the current was kept constant at 0.16 µA/cm@super 2@. The coating thickness on particles was modeled by assuming a uniform flux depositing over a spherical powder surface. Spatially resolved electron energy loss was calculated to predict the CL intensity versus beam energy and incident angle relative to the local surface normal. The predictions of the CL intensity versus incidence angle, coating thickness, and primary beam energy agreed well with experimental data. The consequences of these data relative to phosphor degradation and low voltage efficiency will be discussed.

10:00am **FP-TuM6 Effect of He/Ar Sputtering Gas Mixture on the Brightness of RF Magnetron-Sputtered ZnS:TbOF for Alternating Current Electroluminescent Displays***, **J.P. Kim**, M. Davidson, D. Moorehead, P.H. Holloway,* University of Florida

ZnS:TbOF has shown promise as a green electroluminescent phosphor. We have studied the effects of He/Ar mixture as ambient gas on the brightness of ZnS:TbOF thin film electroluminescent devices. ZnS:TbOF phosphor films were planar magnetron sputter deposited from consolidated powder targets of ZnS:TbOF (1.5 mol %) at 120W. All films were deposited at a substrate temperature of 160°C and total pressure of He/Ar gas was kept at 20mTorr. Helium gas ratio was changed from 0% to 70%. Top insulator layer was planar magnetron sputter deposited from consolidated powder targets of BaTa@sub 2@O@sub 6@. The sputtering deposition rate of ZnS:TbOF was in the range of 84Å/min - 113Å/min and was not changed significantly by increasing the He/Ar ratio. He/Ar gas mixture up to 50% He don't result in any significant change of the brightness (B@sub 40@@super half@) of half stack structures (bottom dielectric layer and top Al dot contact directly on the ZnS:TbOF) for either as-deposited or annealed films (500 °C,60 min). At a higher helium ratio (> 60%), the B@sub 40@@super half@ decreased for both as-deposited and annealed films (500 °C, 60 min). Surface roughness was less for >60% He, as measured by Atomic Force Microscopy (AFM). Full Width of Half Maximum (FWHM) from X-ray diffraction showed increased crystallinity of deposited film > 60% He. Films deposited at > 60% He exhibited higher dielectric constants. Therefore, the brightness decrease in high helium is attributed to reduced roughness and increased dielectric constant of the phosphor layer. This work was supported by DARPA Grant MDA 972-932-1-0030 through the Phosphor Technology Center of Excellence.

10:20am **FP-TuM7 Eu@super +3@ and Cr@super +3@ Doping for Red Cathodoluminescence in ZnGa@sub 2@O@sub 4@***, **J.J. Peterson**,* Advanced Vision Technologies, Inc.*; P.D. Rack,* Rochester Institute of Technology*; M.D. Potter,* Advanced Vision Technologies, Inc.

Cathodoluminescence (CL) emission spectra and photoluminescence (PL) excitation spectra were used to evaluate Eu@super +3@ and Cr@super +3@ as activators for red luminescence in ZnGa@sub 2@O@sub 4@. In the Eu@super +3@ doped ZnGa@sub 2@O@sub 4@ materials blue host emission was observed at high current densities and is attributed to ground state depletion of the Eu@super +3@ activators. In addition, PL excitation measurements revealed poor energy-transfer from the ZnGa@sub 2@O@sub 4@ host to the Eu@super +3@ ions. Cr-doping resulted in a saturated red-color and no host emission was observed over the entire current density regime investigated. The PL excitation of the ZnGa@sub 2@O@sub 4@:Cr@super +3@ revealed good overlap between the host emission and the O-Cr@super +3@ ligand-to-metal charge transfer absorption band. Cathodoluminescence efficiency and emission spectra of various compositions will be presented as a function of current density. The relevant energy transfer theory for the red emission in Eu@super +3@ and Cr@super +3@ doped ZnGa@sub 2@O@sub 4@ will be discussed. Finally, a process that integrates Cr@super +3@ (red), Mn@super +2@ (green) and intrinsic ZnGa@sub 2@O@sub 4@ (blue) into a single thin film for high-resolution field emission display applications will be shown.

10:40am **FP-TuM8 Molecular Organic Light-Emitting Devices based on a Guest-Host System***, Z.H. Kafafi, **H. Murata**, L.C. Picciolo,* Naval Research Laboratory **INVITED**

This talk will review the molecular and electronic properties of the guests and hosts used in the active emissive layers in molecular organic light-emitting devices (MOLEDs), and the electrical and luminescent characteristics of MOLEDs with high efficiency, good thermal stability and extended lifetime. Saturated red, green and blue (RGB) emission based on a common host will be discussed in terms of energy transfer from the host to the guest molecules, and direct electron-hole recombination on the highly luminescent guest molecules. The mechanisms leading to high electroluminescence quantum efficiency and, good thermal and temporal stability will be discussed.

11:20am **FP-TuM10 Aging and Luminescent Characterization of Coated ZnS:Ag Phosphors in FED Systems***, **G.R. Villalobos**, J.S. Sanghera, I. Aggarwal,* Naval Research Laboratory

Sulfide phosphors used in field emission displays (FED) tend to degrade (both physical and luminescent degradation) from interaction with the emitted electrons and residual gases in the device vacuum. A variety of coating types may protect the phosphors from degradation. For example, inert buffer coatings can isolate the phosphor from the residual gases in the device vacuum, electrically conductive coatings can reduce the surface charging, and thermally conductive coatings could reduce the heating from the electron beam on the phosphor surface. It is also possible that a layered structure composed of these individual coatings could be of benefit. We have scaled up a process that we developed to hermetically coat individual phosphor particles with various films. Whereas the laboratory-sized process could coat a half-gram of phosphor per day, the pilot plant scale system can coat up to 100 grams per day without a reduction in luminescent properties. To date we have deposited SiO@sub 2@, MgO, ITO, and Na(PO@sub 3@)@sub 6@ coatings on ZnS:Ag phosphors. The process allows a precise control over the thickness of the coating. Coating thicknesses of 5 to 90nm have been achieved. The process is continuous, is fully automated, and further scaleable to industrial sizes. The cathodoluminescent (CL) efficiency and aging behavior of the SiO@sub 2@ coated phosphor has been measured in both laboratory and FED devices. Aging tests have shown a dramatic improvement in aging behavior between the coated and un-coated phosphors. While phosphor efficiency and chromaticity are within 10% of uncoated values. Future work will include the measurement of the other coating materials.

11:40am **FP-TuM11 Temperature Dependence of Cathodoluminescent Degradation of ZnS Phosphor***, **B. Abrams**,* University of Florida*; W. Roos,* University of the Orange Free State*; L.C. Williams, P.H. Holloway,* University of Florida

The effect of temperature on ZnS:Ag,Cl cathodoluminescent (CL) intensity and degradation by surface chemistry changes has been investigated using an Oriel optical spectrometer and a scanning Auger electron spectrometer. With vacuum pressures maintained between 3-5x10@super-9@ Torr, thermal quenching has been measured on the ZnS:Ag,Cl powder pressed into an Al cup and mounted onto a heater stage. Using a 2kV accelerating voltage, a constant current of 5µA and a 1mm spot size, the sample temperature was incrementally increased to 400@supero@C with CL and AES measurements being taken after each increase. AES data show little change in the S, Zn, O and C peaks on the surface as the temperature is increased. There is also no significant shift in Auger peak energies with temperature. The CL brightness decreased dramatically at T@>=@300@supero@C, while the maximum CL peak intensity shifted from 450nm to almost 600nm. CL brightness measurements taken as the sample was incrementally cooled back towards room temperature showed that the most intense CL peak shifted back to 450nm. However, a large hysteresis was observed in the CL intensity versus temperature data due to poor heat transfer. Recovery of the CL intensity upon returning to RT ranged from 70% recovery to 100% recovery dependent upon the hold time at each temperature. The mechanisms for these effects will be discussed. This work was supported by DARPA Grant MDA 972-93-1-0030 through the Phosphor Technology Center of Excellence.

Incorporating Principles of Industrial Ecology
Room 304 - Session IE-TuM

Methods of Industrial Ecology Analysis / Global Concerns

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

9:00am **IE-TuM3 The 21st Century Co-Evolution of Technology and Environmental Science***, **T.E. Graedel**,* Yale University **INVITED**

Technology, traditionally seen as the enemy of the environment, is likely to be a positive environmental force in the 21st century, and not only through its application to feed the 8-12 billion people that will occupy the planet. Technology is also likely to be central to improving overall quality of life. Nevertheless, 21st century technology will have to consider the potential environmental impacts of its every action. The process of so doing, termed industrial ecology, is rapidly entering planning, product design, and customer response activities throughout the world. Industrial ecolgoy works in cooperation with environmental science, and incorporates new environmental knowledge in its decision-making processes. The tools of industrial ecology, including life-cycle assessment, design for environment, and materials flow analysis reveal that the potential benefits to both corporations and the environment of optimizing technology-environment interactions are substantial. Some examples of such optimization will be presented and discussed.

9:40am **IE-TuM5 Single Particle Analysis of Particulate Pollutants in Yellowstone National Park and Hawaii Volcanoes National Park*, R.E. Peterson,*** *B.J. Tyler,* Montana State University

Particulate pollution is a complex mixture of organic and inorganic compounds which includes a wide range of sizes and whose composition can vary widely depending on the time of year, geographical location, and both local and long range sources. Particles greater than 2 micrometers in diameter are generally formed by mechanical processes while smaller particles are formed by gas to particle conversion and accumulation/coagulation. Because particles smaller than 2.5 micrometers can become trapped deep in the lungs, it is of particular interest to identify toxic substances, such as heavy metals and polyaromatic hydrocarbons, that may be present in particles of this size range. We are evaluating the potential for using TOF-SIMS to study the composition of single particles from atmospheric aerosol. For this study, samples of naturally occurring and anthropogenic atmospheric aerosol were collected at the west entrance to Yellowstone National Park (YNP) during the winter snowmobile season of 1998/99. During the winter snowmobile season, incomplete combustion products from snowmobile exhaust may be a predominant source of airborne particulate matter in YNP. In Hawaii Volcanoes National Park (HVNP), lava flows from the ongoing Kilauea volcano eruption are a particulate source which has been little investigated. Aerosol near fresh pahoehoe flows was sampled in January and May of 2000. Graseby/Anderson cascade impactors were used to collect size segregated fractions of the aerosol onto aluminum substrates in YNP and onto gold coated substrates in HVNP. Sections of the substrates have been imaged using a PHI TRIFT I instrument with a Ga primary ion source. Both positive and negative ion images have been studied. A large number of particles could be distinguished on the impactor surfaces. Multivariate methods, including mixture models and principal components analysis have been employed to enhance image resolution and aid in interpretation of the SIMS images.

10:00am **IE-TuM6 Environmental Concerns in Brazil*, T.M. Tavares,*** Federal University of Bahia (UFBA), Brazil **INVITED**

Brazil has not reached the phase of concern for industrial ecology. Society has not even been able to practice selection of solid wastes in a broad sense. Industries are now concerned on obtaining ISO14000 certificate and adopting clean technologies. In a capitalist society the main driving force is economic interest. The means available to society to protect the environment are government regulation/ law enforcement and consumers demand. In Brazil the frame of the legislation for environmental management is closer to that of Europe than of USA. It includes a good and often efficient system of licensing installation of new enterprises and operation of existing ones. A great number of large ecological reserves have been established. However two things are lacking: proper criteria for a great number of chemical pollutants and law enforcement. National consumer's demands have concentrated on protection of natural reserves and on industrial emission reduction. Demands of international consumers have resulted in cleaner production, as in pulp industries with change to elemental chlorine free (ECF) or total chlorine free (TCF). Brazil as a whole has no tradition in development of technologies. First, it lacks both financial and trained human resources since society never demanded it. This has also not been a concern of the government until 1999, when a new program for development of technologies has been launched ; Secondly, not before recently, part of the restricted development of technology in the country aimed green production. However, when government takes the initiative and demands new technology to meet economic interest, society responds. In 1970, 80% of the oil consumed in Brazil came from abroad, and the international prices were rising. With incentives from the Government, ethanol was introduced as fuel and new motors were development. Although the economic interest was the driving force, the environment profited from this less polluting fuel, and now other countries are adopting it. International demands can play an important role, and may be able to introduce carbon fixation through incentives, to more recycling, to assessment of life-cycle of products and to a greater environment conscious attitude.

10:40am **IE-TuM8 Multi-phase Atmospheric Chemical Processes: A Major Gap in Understanding Regional to Global Air Pollution Issues*, L. Barrie,*** Pacific Northwest National Laboratory **INVITED**

Chemicals from natural or anthropogenic activities that are released to the atmosphere as gases or particles are dispersed and transported on the winds. Their residence time and hence, range of influence, is determined by the processes of chemical and physical transformation, air-surface exchange and precipitation scavenging. Multi-phase chemistry involving interactions of gases with solids or liquids in the atmosphere or at the Earth's surface is often a major obstacle in understanding environmental chemical cycles and hence establishing effective pollution abatement strategies. There are a variety of pollution issues operating on a range of scales from local to global that threaten the quality of life on this planet. They include: urban smog (e.g. ozone and particulate matter), regional acidification/toxification and visibility reduction, global stratospheric ozone depletion and climate change. An understanding of multi-phase reactions is complicated by the largely unknown, highly variable nature of liquid/solid particles in the atmosphere. These include atmospheric aerosols (0.001 to 10 micrometers), cloud droplets and ice (1 to 20 micrometers) and rain/snow particles (20 to 20000 micrometers). They range greatly in composition and ionic strength (6x10@super -6@ to 10 molal). The interaction of gases with particles involves unreactive phase-partitioning processes as well as reactive kinetic processes. In the case of persistent semi-volatile substances such as herbicides, pesticides and polycyclic aromatic compounds, the environmental pathways are often dominated by the former process, In contrast, many substances are chemically produced or transformed during gas-particle interactions. There is a need to understand the nature of organic compounds in atmospheric particles and the basic physical chemistry of the interaction of these mixtures with water vapour and other gases.

11:20am **IE-TuM10 Structure and Composition of Size- and Time-Resolved Outdoor Aerosols Determined Using TOF-SIMS*, D.J. Gaspar,*** *M.A. Carpenter, J.P. Cowin, D.R. Baer,* Pacific Northwest National Laboratory

The study of aerosol particles has been identified as a top priority in atmospheric research due to their importance as heterogeneous reaction sites and the potential health consequences of particulate inhalation. Aerosols are known to have highly variable composition, with non-volatile, semi-volatile, and volatile organic and inorganic constituents. Although much work has been done recently, further understanding of structure and composition remains important. Thus, the composition of outdoor aerosols have been investigated using time-of-flight secondary ion mass spectrometry (TOF-SIMS). Particles were collected using a multiple stage impactor, which time tagged and sorted incident particles from 0.1 to 10 microns into discrete size ranges. A PHI TRIFT TOF-SIMS instrument was used with a Ga@super +@ liquid metal ion gun (LMIG) for both depth-profiling and analysis, and a Cs@super +@ ion source for more extensive depth-profiling. Mass spectra for both negative and positive secondary ions were obtained for the time- and size-sorted particles. Data was obtained for both collections of particles and a number of individual particles. The mass spectra have been analyzed to determine the inorganic and organic fractions of the aerosol particles. Three-dimensional molecular and atomic maps have been constructed for key environmentally important components of several characteristic particles. We relate the composition to environmental factors such as daylight and road traffic, and inferences are drawn concerning sample chemical history.

Material Characterization
Room 207 - Session MC-TuM

Real World Surface Analysis

Moderator: A. Belu, Physical Electronics

8:20am **MC-TuM1 Surface Interaction, Coverage and Performance of Quaternary Amine Treatments on Hair*, B.C. Beard,*** Akzo Nobel Chemicals*; D. Tang,* Akzo Nobel Surfactants America*; J. Hare,* Akzo Nobel Chemicals

Surface analysis by Xray Photoelectron Spectroscopy (XPS) has shown specific one to one (ionic) interaction between cationic quaternary alkyl conditioning molecules and the anionic sulfonate groups present on the hair surface. Conditioning cationic quaternary molecules incorporating ester and alcohol functionality (ester quat) demonstrate a lower number of surface quaternary nitrogen per sulfonate group, indicating an altered surface interaction mechanism. Relative conditioner surface coverage for the ester quat is not reduced despite the apparent decrease in ionic interaction at the surface. Molecular dynamics modeling of the conditioner-hair surface interaction indicate higher adsorption energies for ester quaternary amine conditioning molecule. Industry standard tests demonstrate the superior performance of ester quats, in keeping with the increased surface coverage.

8:40am **MC-TuM2 Chemical Characterization of Modified Nanotips by TOF-SIMS and Laser-SNMS***, **R. Kamischke**, F. Kollmer,* Physikalisches Institut der Universitaet Muenster, Germany*; R. Stark, W. Heckl,* Institut fuer Kristallographie und Mineralogie der Universitaet Muenchen, Germany*; A. Benninghoven,* Physikalisches Institut der Universitaet Muenster, Germany

For many applications of nanotips detailed information on their chemical surface composition with high sensitivity is a key issue. This holds e.g. for their use as chemical sensors, where the tip surface is chemically modified, or for nanoextraction of sample material by direct contact with the tip. TOF-SIMS and Laser-SNMS are the most sensitive techniques for chemical surface mapping with high lateral resolution. The large fraction of sputtered neutrals and their efficient Laser-postionization results in a high Laser-SNMS sensitivity. In this contribution we summarize and compare results of TOF-SIMS and Laser-SNMS characterization of chemically modified as well as metal loaded Si@sub 3@N@sub 4@ and Si AFM cantilever tips. All experiments were carried out in a reflectron based time of flight instrument with a fine focused Ga@super +@-LMIS (@>=@80 nm). For nonresonant postionization an excimer laser (248 and 193 nm) was applied. Special efforts had to be put on the sample preparation. Distortion of the extraction field, shadowing effects, charging, and presputtering during sample adjustment had to be reduced to a minimum. On surface modified cantilevers it is not possible to characterize the tip itself, because of the lateral resolution being limited to at best 80 nm. However, imaging the tip pyramid provides detailed information on the surface composition, and in this way on the results of surface modification efforts. For Nanoextraction of metals (Co, Cu, Ag) the sample is imaged by AFM and material is extracted by applying a loading force of several µN and scanning over the surface for some µm. The extracted amount of material adhering to the top of the tip can be characterized down to the sub-amol range. Most important advantages of Laser-SNMS compared to SIMS are enhanced ion yields for elements (@<=@10@super -2@), the ease of quantification and the fact that sputtered neutrals are not affected by electrostatic fields in the vicinity of the sample.

9:00am **MC-TuM3 Real World Surface Analysis***, **B. Hagenhoff**,* TASCON GmbH, Germany **INVITED**

Most surface analytical techniques like photoelectron spectroscopy (XPS) and secondary ion mass spectrometry (SIMS) have left their academic origins and are routinely applied in university and industry laboratories. Whereas in former times most analyses were performed at model systems having only one or few known compounds, nowadays surface analytical techniques are used to solve daily occurring problems in industrial environments. Materials to be analyzed in these cases mostly contain several components and the respective samples may have undergone additional surface treatments. The talk will concentrate on the special requirements to be dealt with when working on practical problem solving. Issues covered will include sample preparation, selection of the suited analytical technique, set-up of the equipment and data evaluation. Case studies taken from semiconductor and glass industry will be used to explain how both, XPS and TOF-SIMS, can successfully be used to solve "real world" problems.

9:40am **MC-TuM5 Thermal Degradation of IM7/BMI5260 Composite Materials: Characterization by X-ray Photoelectron Spectroscopy***, **S. Ohno**, M.-H. Lee, K.Y. Lin, F.S. Ohuchi,* University of Washington

High performance polymeric composites (IM7/BMI5260) are being considered for use in structures for high speed aerospace vehicles. In this application, composite components are exposed to elevated temperatures for a long time period. This results in physical and chemical degradation of the polymers. In this paper, experimental studies were conducted to investigate the effects of isothermal aging of the IM7/BMI5260 exposed at 150 - 200°C using x-ray photoelectron spectroscopy (XPS). During the XPS measurements, binding energies for the carbon-fibers are uniquely determined because of their electrically conducting nature, whereas binding energies for the polymeric matrix are shifted by the amount of bias voltage applied to an electron flood gun. This effect turns out to be useful to separate out the contribution from carbon fibers and polymeric matrix, thus we have established a unique experimental protocol to analyze the composite material surfaces. Experimentally, the composite specimens were oxidized in an environmental cell specially designed to mimic the aging conditions, and analyzed to learn intrinsic nature of the chemical reactions. These data were further compared with those obtained from long-aged specimen (7 months at 205 °C in air). Our results indicate that degradation of the IM7/BMI5260 is initiated by preferential oxidation of the carbon sites in the BMI to form the carbonyl species, followed by the oxidation to CO@sub2@ leading to degradation.

10:00am **MC-TuM6 Pt-Metal Oxide Aerogel Catalysts: An X-ray Photoemission Investigation***, **A.J. Nelson**, J.G. Reynolds,* Lawrence Livermore National Laboratory

X-ray photoemission spectroscopy was used to study Pt-metal oxide aerogel catalysts that have been developed to respond to increased NO@sub x@ emissions of lean-burn engines. Lean-burn engines, critical components of low and zero emission vehicles, produce much higher levels of engine-out NO@sub x@ and current three-way catalytic converters are not sufficient to meet Clean Air Act standards. Platinum catalysts were formed by the reaction of modified Pt coordination compounds with selected transition-metal alkoxides through sol-gel techniques into aerogels. Photoemission measurements on the valence band electronic structure and Pt 4f, Si 2p, Ti 2p and O 1s core lines were used to evaluate the chemistry of the material after each processing step. Results indicate Pt-O bonding and reduced Pt disbursed in the aerogel. In addition, Si 2p, Ti 2p and O 1s binding energies indicate an oxo-bridged network structure.

10:20am **MC-TuM7 Quantification of the Changes in the Air-formed Oxide/Hydroxide Film at the Surface of Aluminium on Exposure to Ambient Conditions***, **M.R. Alexander**, G.E. Thompson,* UMIST, UK*; G. Beamson,* RUSTI, CLRC, UK*; A.J. Roberts,* Kratos Analytical, UK

The performance of coated and bonded Al is dependent on its surface chemistry. XPS is a powerful tool for characterising of the surface air-formed film. It is apparent that agreement exists in the literature on the method to calculate the oxide thickness from the clearly resolved metal and oxide components of the XPS Al2p core level.@footnote 1@ However, there is no consensus on the approach for fitting the unresolved oxide and hydroxide components of the O1s, indeed some suggest that it is not advisable.@footnote 2@ Recently, a method based on defining the separation between the O1s and Al2p components has been developed using an oxyhydroxide standard.@footnote 3@ Here, the film formed at the surface of magnetron sputtered Al is characterised. Importantly, this sample allows reliable definition of the age of the surface film and control of the alloying elements. Curve fitting of the O1s and Al2p core levels from samples after a range of atmospheric exposure times revealed the gradual formation of hydroxide ions in the surface film, an increase in its thickness and the adsorption of adventitious hydrocarbon. Interestingly, it was determined that atmospheric moisture influences strongly the hydroxyl concentration and the rate of film growth. Changes in the wetting of the surface were measured through the water contact angle, which increased from about 10° to 80° over a 24-h period. This was assigned to the formation of a continuous overlayer of hydrophobic adventitious hydrocarbon onto the hydrophilic oxide/hydroxide surface film. Characterisation of this "ageing" of the Al surface forms the basis for an investigation into the effectiveness of plasma cleaning and the atmospheric stability the resultant surface. @FootnoteText@ @footnote 1@ B Strohmeier Surf. Interface Anal. 15 51 (1990). @footnote 2@ PMA Sherwood Surf. Sci. Spect. 5 (1) 1 (1998). @footnote 3@ MR Alexander, GE Thompson and G Beamson, Surf. Interface Anal., 29 (7) in press (2000).

10:40am **MC-TuM8 Scanning Auger Microscopy Studies of an Ancient Bronze***, **E. Paparazzo**,* Consiglio Nazionale delle Ricerche, Italy*; A.S. Lea, D.R. Baer,* Pacific Northwest National Laboratory*; J.P. Northover,* University of Oxford, UK

We have conducted a scanning Auger microscopy (SAM) analysis on a Syrian bronze of the early I millennium BC. The objective was to derive a picture of modifications of the object's surface composition, induced by chemical attack by the ambient. Understanding degradation of ancient materials dating from a well-defined historical context provides information about long-term corrosion phenomena that is not possible from laboratory data. Such information is also useful for restoration and conservation efforts. While corrosion processes in the bulk are understood, this is not true for localized intergranular and transgranular surface corrosion in these materials. This requires information about local chemical composition and movement of ionic species that has not generally been available, and we find AES useful in accomplishing this task. SAM images of Cu, Sn and O, ~ 100-nm spatial resolution, and Auger point spectra show that Sn acts as a barrier against O@sub 2@ attack, as it entirely traps this gas into a SnO@sub 2@-like oxide, thus minimizing copper oxidation. Submicron spectromicroscopic evidence is given that S-induced corrosion occurs mainly via chemical attack along grain boundaries, where Sn has a low abundance and copper sulfides are detected. Lateral segregation of Sn and Cu domains is imaged with a spatial resolution of 15 nm. This result marks the best spatial resolution any analytical method has yet achieved in highlighting lateral chemical heterogeneities of ancient bronzes. Although archaeomaterials lie outside the mainstream applications of Auger techniques, this study provides convincing evidence that SAM can greatly advance our understanding of these materials.

11:00am **MC-TuM9 Practical Applications of Surface Analysis Techniques in Electroplating*, C. Xu*,** *J.A. Abys,* Lucent Technologies

Electroplating has been widely used to deposit thin metal films on various substrates either to achieve certain functionality (wear resistance, solderability, wire bondability, corrosion resistance) or specific appearance. The materials properties are critical to the functionality and are dependent on the electroplating process. These properties are determined by the elemental, and chemical composition, and deposit structure. Surface analysis techniques are unique in their ability to provide specific diagnostic tools to study electrodeposited films. In this paper, the potential of various surface analysis techniques for investigating failure modes and new products development in electroplating industries will be discussed and demonstrated using various case studies. A comparison of techniques such as AES and XPS to traditional failure mode analysis methods such as Scanning Electron Microscopy (SEM) will be made.

11:20am **MC-TuM10 Surface Chemistry and Physical Properties Related to Adhesion of Various Soldermask Materials*, C.A. Bradbury*,** *Y. Du, T. Jiang,* Micron Technology Inc.

In Flip Chip (FC) Ball Grid Array (BGA) packages, adhesion between soldermask material to mold compound, underfill and liquid encapsulant materials are critical to package reliability. Delamination will result in package crack and solder joint failure. In this study, the adhesion of several different types of soldermask materials to an underfill polymeric material was evaluated. The surface chemical properties of the soldermask materials were characterized using x-ray photoelectron spectroscopy (XPS) and surface tension test. The surface chemistry was correlated to the interfacial fracture toughness obtained by Mixed Mode Bending (MMB) test.

Magnetic Interfaces and Nanostructures
Room 206 - Session MI+NS+NANO 6-TuM

Magnetic Imaging I

Moderator: M. Miller, Naval Research Laboratory

8:20am **MI+NS+NANO 6-TuM1 Scanning Electron Microscopy with Polarization Analysis (SEMPA) Imaging of Surface and Thin Film Magnetic Microstructure*, J. Unguris,*** National Institute of Standards and Technology **INVITED**

Scanning Electron Microscopy with Polarization Analysis (SEMPA) provides a direct image of a sample's magnetization by measuring the spin polarization of secondary electrons emitted in a scanning electron microscope (SEM). SEMPA therefore generates a high resolution picture of the direction and relative magnitude of the magnetization, in the same way that an SEM images topography by measuring the secondary electron intensity. With submomolayer magnetic sensitivity and probe sizes as small as 10 nm, SEMPA is sensitive to extremely small amounts of magnetic material. In particular, SEMPA's surface sensitivity makes it especially well suited for the direct, quantitative mapping of the magnetization direction in thin films and at the surface of magnetic materials. Comparisons between magnetic and physical structure in these systems are further facilitated by the natural ability of SEMPA to separate the magnetic and topographic contrast. When combined with other compatible surface analytical techniques such a Auger, RHEED and STM, SEMPA can also provide information about the relationship between the magnetic structure, the chemical structure, and the atomic scale order. SEMPA can also be used for real time, in situ imaging of magnetic structure during thin film growth and processing. This talk will describe the SEMPA technique by presenting examples of measurement applications from thin film and multilayer magnetism, surface magnetism of ferromagnets and antiferromagnets, and depth profiling of magnetic structures in multilayers. These measurements have provided a better understanding of thin film domain structures, spin reorientation transitions, interlayer exchange coupling, magnetic ordering in antiferromagnetic films, and the relationship between magnetic domain structure and magnetoresistance in multilayers.

9:00am **MI+NS+NANO 6-TuM3 'Magnetic-Laboratory' on an AFM Tip*, B.K. Chong*[1]**, *H.P. Zhou,* University of Glasgow, UK, United Kingdom*; G. Mills, L. Donaldson, J.M.R. Weaver,* University of Glasgow, UK

We present novel magnetic nanosensors based on the functionalisation of an AFM probe for use in measuring, imaging and manipulating magnetic specimens. The probes are fabricated using bulk silicon micromachining and electron-beam nanolithography (EBL). The use of conventional lithographic techniques and a microfabricated substrate allows the batch production of a large number of similarly functionalised probes without the need for individual processing of single probes and hence gives very good reproducibility.@footnote 1@ We have demonstrated two classes of magnetic probe. The eMFM probe is one in which the permanent magnetic coating used in conventional MFM tips is replaced by a small electro-magnetic coil to form a magnetic-sensitive AFM tip. Initial results indicate controllability of coil size (spatial resolution) to 1/4 µm diameter, demonstrated capability of magnetic imaging and possible application in local magnetic modification. The Hall bar magnetometer for SHPM, is also integrated with a tip and cantilever. This involved the development of a new fabrication technique in which the resist was supported by a lattice of sacrificial structures which spanned the spaces between probes. This allowed the use of low melting point or chemically reactive materials as the sensor. The combination of eMFM and Hall bar magnetometer forms a novel type of magnetic sensor-actuator probe, a 'Magnetic-Lab' on a tip. Such a probe will allow the magnetic imaging of a specimen without significant distortion due to stray fields from the probe using Hall probe magnetometry as well as the deliberate modification of its magnetic state using the coil. @FootnoteText@ @footnote 1@ H.Zhou, G.M. Mills, B.K.Chong, L. Donaldson & J.M.R. Weaver, 'Recent Progress in the Functionalisation of AFM Probes using Electron-Beam Nanolithography', J. Vac. Sci. Technol. A17(1) 2233-9(1999).

9:20am **MI+NS+NANO 6-TuM4 High Anisotropy, High Gradient Magnetic Tips For Magnetic Resonance Force Microscopy*, H.J. Mamin*,** *B.C. Stipe, C.S. Yannoni, D. Rugar,* IBM Almaden Research Center*; T.D. Stowe, T.W. Kenny,* Stanford University*; D. Streblechenko, M.R. Scheinfein,* Arizona State University

In magnetic resonance force microscopy (MRFM), imaging is performed by detecting forces on a magnetic tip, but arising from only those spins within a thin resonant slice. To achieve the ultimate goal of single-spin detection, the tip must produce sufficient field gradients, at least 10 G/nm. At the same time, thermal fluctuations in the tip moment must be sufficiently small that the tip does not perturb the spin under study. These requirements have driven us to the use of tips based on high anisotropy, rare-earth bulk magnets. Small particles of NdFeB, PrFeB, and SmCo have been attached to cantilevers and oriented in an external magnetic field. The particles were then sculpted to the desired sub-micron size and shape with a focused ion beam. The magnetic properties have been characterized through cantilever-based magnetometry as well as electron holography. By measuring dissipation and applying the fluctuation-dissipation theorem, we have set upper limits on the low frequency fluctuations in the tip moment. Using a tip optimized for a 1 nm slice thickness, we have detected MRFM signals from on the order of 100 net spins. This work is supported, in part, by the Office of Naval Research.

9:40am **MI+NS+NANO 6-TuM5 Quantitative Magnetic Force Microscopy and Exchange Force Microscopy: New Tools for Magnetic Imaging*, H.J. Hug*,** *P.J.A. van Schendel, S. Martin, R. Hoffmann, P. Kappenberger, M.A. Lantz, H.-J. Guentherodt,* University of Basel, Switzerland **INVITED**

Magnetic Force Microscopy has become a a well established technique for studying the topography and the micro-magnetic structure of various samples with a high lateral resolution. Among these are ferromagnetic and superconducting materials, and magnetic recording read/write-heads. Recently there has been growing interest in the quantitative analysis of measurement data obtained using a magnetic force microscope (MFM).@footnote 1@ Recent tip calibration procedures allow quantitative stray field measurements, the determination of the stray field distribution of the tip, and its stray field sensitivity. The best lateral resolution currently is around 30nm. However, the combination of ultra-sharp SFM-tips coated with ultra-thin magnetic layers and improved instrumental sensitivity may allow a lateral resolution around 10nm. A higher lateral resolution may be reached by the measurement of exchange forces. The principles of this new

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[1] **Falicov Student Award Finalist**

technique and first experiments will be discussed.@FootnoteText@@footnote 1@P.J.A. van Schendel et al., J. Appl. Phys. 88, 435-445 (2000)

10:20am **MI+NS+NANO 6-TuM7 Magnetic Force Microscopy of Coupled and Decoupled Micrometer Scale Permalloy Structures***, **U. Memmert**, A.N. Müller, U. Hartmann,* University of Saarbrücken, Germany*; J. Jorzick, C. Krämer, S.O. Demokritov, B. Hillebrands,* University of Kaiserslautern, Germany*; E. Sondergard, M. Bailleul, C. Fermon,* CEA Saclay, France

The magnetic structure and the magnetization reversal process of arrays of micron size rectangular magnetic permalloy islands were investigated by magnetic force microscopy in external magnetic fields. The samples were prepared by e@super -@-beam lithography and ion etching of UHV deposited 35 nm thick permalloy films. Islands of 1 µm x 1.75 µm dimensions were investigated with inter-island spacings between 0.1 µm and 1 µm. The data show a transition from not interacting islands for large inter-island spacing to interacting islands for the smallest spacing. For not interacting islands flux-closure structures were found to be present without external fields. Either a simple Landau structure with one single cross-tie within in the 180° wall or diamond structures consisting of 90° walls were found. For interacting islands the individual structures were often found in a magnetized state even in zero field. Edge domains were present on both short edges of each structure. A demagnetization of the interacting islands in an ac-magnetic field along the longer axis of the islands leaves the individual structures in a magnetized state with edge domains. Within the rows along the long island axis all structures are magnetized in the same direction. The rows show a row by row alternating magnetization resulting in a net zero magnetization for the entire sample. A demagnetization in an ac-field perpendicular to the long axis leaves each individual structure in a individually demagnetized state. Magnetization reversal for external fields along the long island axis takes place by simultaneous switching of structures being located together in the same row within the pattern.

10:40am **MI+NS+NANO 6-TuM8 Correlation of Structural and Magnetic Properties of Fe/Cr(001) Studied by Combined SP-STM and MFM***, **M. Kleiber**, R. Ravlic, M. Bode, R. Wiesendanger,* University of Hamburg, Germany

The magnetic structure of ultrahin Fe films on the (001)-surface of a chromium single crystal is the result of the competition between the antiferromagnetic coupling to the alternately magnetized Cr(001)-terraces and the ferromagnetic coupling in the iron layer. It is expected that for thin Fe-films the antiferromagnetic coupling between the Cr-substrate and the Fe-overlayer dominates the surface domain structure while Fe-exhibits a single-domain state for thicker films. By combining STM, spin-polarized STS and UHV-MFM we have correlated the structural and magnetic properties of the Fe/Cr(001) system. These microscopic techniques reveal that the domain structure depends on the local step density. On areas with high step density no domains are found which is expected as the terraces are too small to induce domains in the iron film. In contrast a low step density leads to a domain structure of the Fe-film which is directly linked to the step structure of the underlying Cr-substrate.

11:00am **MI+NS+NANO 6-TuM9 Flux Lattice Imaging of a Patterned Nb Film with a Cryogenic Magnetic Force Microscope***, **M. Roseman**, P. Grutter,* McGill University, Canada*; V. Metlushko,* Argonne National Laboratory

Using our cryogenic magnetic force microscope, we have investigated a superconducting Nb thin film, 100 nm in thickness with T@sub c@ ~6.6 K. The film is patterned with a square array (1 µm by 1 µm) of antidots, which serve as artificial pinning centers for magnetic flux. We have observed the flux lattice as a function of temperature (5.5 K - 6.6 K) and applied magnetic field, for field strengths up to 62.1 G, the third matching field (a matching field is one where the flux lattice spacing is commensurate with the antidot array). Evidence of flux dragging by the tip reveals information about both tip-vortex and vortex-vortex interactions, and provides an indication of localized sample pinning potentials. Force distance curves acquired at temperatures near T@sub c@ clearly demonstrate an observable Meissner force between tip and sample, and allow for an estimation of the value of the temperature dependent London penetration depth, @lambda@@sub L@(T).

11:20am **MI+NS+NANO 6-TuM10 Magnetic Field Measurements of Current-Carrying Devices by Force Sensitive Magnetic Force Microscopy with Potential Correction***, **R.A. Alvarez**, S.V. Kalinin, D.A. Bonnell,* University of Pennsylvania

Magnetic force microscopy (MFM) is a well-known technique based on the detection of the dynamic response of a mechanically driven cantilever to a magnetic field. MFM image contrast of non-conductive or biased surfaces includes contributions of electrostatic forces that can in some circumstances dominate the total force gradient. Since current-carrying devices, e.g. lines or circles are recognized as convenient calibration standards to determine first and second order magnetic moments of the MFM probes, this ambiguity is not inconsequential. An approach to imaging is proposed that combines surface potential nulling measurements with magnetic force microscopy to eliminate the electrostatic forces. Unlike conventional MFM, this technique measures force rather than force gradient. The distance, line bias and modulation frequency dependence of cantilever response was found to be in excellent agreement with magnetostatic calculations. Based on these observations, a new type of MFM on current carrying devices is proposed. In this technique, the device is ac biased at the off-resonant frequency and the current induced magnetic field results in cantilever deflection. At the same time, ac voltage bias at the resonant frequency is applied to the tip and conventional SSPM feedback is used to match tip and surface potentials. This technique allows simultaneous collection of surface potential and magnetic force images. To the best of our knowledge, this is the first example of an SPM technique that utilizes simultaneous active and passive modulation of the tip and allows simultaneous measurement of magnetic and electrostatic forces.

11:40am **MI+NS+NANO 6-TuM11 Evaluation of MFM for Probing Electromigration Processes***, **R. Yongsunthon**, J. McCoy, E.D. Williams,* University of Maryland

The study of electromigration in metals requires correlation of current densities with the evolution of defects in current-carrying lines. In principle, magnetic force microscopy (MFM) is an appropriate tool for this purpose. Most use of MFM has concentrated upon determining magnetic polarity across magnetic domain boundaries, rather than quantification of magnetic field variation. Such quantification is non-trivial, because the extended nature of the tip-sample interaction involves complicated factors such as coupling of the system geometry. To explore the MFM capability to yield reliable analysis, we are evaluating the MFM instrument response for known structures, such as lines containing defects of simple geometry. The instrumental response function is defined by tip parameters, such as tip magnetization and shape, which make predicting the response function impractical. However, it is possible to make meaningful relative quantification and calibration, by comparison with response from structures where the behavior is well understood. To analyze the data from such known calibration samples, the fields around the lines are numerically calculated and compared with deconvolution of the measured signal. Preliminary results suggest that meaningful relative quantification of the signal can be achieved to within 20% and that current variations can be detected to at least 10%. Continuing work to relate this to the limiting levels of current crowding that will be detectable is underway. (Work supported by NSF-MRSEC, grant# DMR 96-3252.

Nanotubes - Science and Applications
Room 309 - Session NM+NS-TuM

Carbon Nanotubes: Synthesis

Moderator: D. Herr, Semiconductor Research Corporation

8:20am **NM+NS-TuM1 Orientated Nanotube Growth with Cobalt Catalyst***, **S. Shah**,* University of Illinois at Urbana-Champaign*; L. Rotkina, H. Choi,* Beckman Institute for Advanced Science and Technology*; J.W. Lyding,* University of Illinois at Urbana-Champaign

Growth of carbon nanotubes (CNTs) is an important area of research in the area of molecular nanotechnology. The full potential of these devices as a building block for nanometer scale structures has not been fully realized and therefore new processing techniques and observations could have impact on the field. This paper will focus on the main aspects of our cobalt catalyst based growth process as well as our observations of the resulting carbon nanotubes. We will then suggest some applications of this technique for the development in the area of nanometer scale research. With the purpose of observing the growth behavior on a Si(100) surface, we have grown carbon nanotubes by means of chemical vapor deposition (CVD). Two distinct types of growth orientations were observed on the surface using a cobalt based catalyst and methane gas as a source of carbon. The first is a series of catalyst islands that have nanotubes growing randomly from them. The patterning of these tubes seems to "bridge" islands of catalyst together. The second growth mechanism is cobalt silicide based, where orientation of both the silicide and carbon nanotubes, appears highly oriented. Growth of oriented CNTs on silicon is particularly important to integrate CNTs with silicon devices. From the observations stated above, we hope to demonstrate a processing technique in which we can grow and characterize nanotubes grown in a highly oriented manner. Finally, our main objective will be to integrate our fabrication techniques to form the basis for the growth of nanotubes of nanometer scale devices.

8:40am **NM+NS-TuM2 Carbon Nanotube Growth on Nanoparticle Catalyst Patterns by Chemical Vapor Deposition***, **J.W. Ward**, P.M. Ajayan, G. Ramanath,* Rensselaer Polytechnic Institute*; L. Kish, R. Vajtar,* Uppsala University, Sweden

Growing nanotubes on catalyst template patterns on flat substrates by chemical vapor deposition (CVD) is a promising approach for creating nano- and meso-scale architectures for a variety of applications such as micro- and bio- electronics devices, and skeletal reinforcements for layered composites. Here, we report the unique morphology and junction-formation potential of CVD-grown carbon nanotubes on catalyst patterns fabricated by a nanoparticle writer. Patterns of Ni, Co, and Ni-Co alloys with different average particle sizes and spatial distributions were prepared on Si substrates and exposed to methane at 1000 °C. Our results show that multiwalled carbon nanotubes grow on nanoparticles. There is a close correlation between the nanotube diameter and the catalyst particle size. The nanotubes exhibit a large number of bends and turns. In several cases, the nanotubes grow from one particle and terminate at another, thereby connecting two nanoparticles lying on the substrate. Based upon our results, we propose a phenomenological explanation for nanotube-bridging. Controlling the formation of such nanobridges could provide a basis for simultaneous selection of both nucleation and termination sites, which is an important requirement for realizing nanotube-based network architectures.

9:00am **NM+NS-TuM3 Carbon Nanotube Catalyst Optimization Using Combinatorial Methods***, **A.M. Cassell**, M. Meyyappan, S. Verma, J. Han,* NASA Ames Research Center

Libraries of liquid-phase catalyst precursor solutions were printed onto various substrates and evaluated for their effectiveness in catalyzing the growth of carbon nanotubes by chemical vapor deposition (CVD) of ethylene. The catalyst precursors were composed of inorganic salt solutions of Al, Si, Fe, Co, Ni, and a removable tri-block copolymer structure-directing agent. Scanning electron microscopy (SEM) was used to rapidly screen the catalyst libraries for activity. The optimized catalysts were then employed in the growth of aligned multi-walled carbon nanotube arrays. Successful implementation of combinatorial optimization methods in the development of high yielding carbon nanotube catalysts is demonstrated, as well as useful techniques for obtaining nanotube films of various configurations.

9:20am **NM+NS-TuM4 Effects Gas Adsorption and Collisions on the Physical Properties of Single-Walled Carbon Nanotubes@footnote 1@***, **P. Eklund**,* Pennsylvania State University **INVITED**

A single-walled carbon nanotube (SWNT) can be thought of as a graphene sheet rolled into a seamless cylinder. They are usually found in bundles containing several hundred tubes, and these bundles present an ideal microporous medium accessible to small gas molecules and ions. For this reason SWNTs are expected to be a sensitive chemical sensor, as has been reported recently. Bundles of SWNTs undergo charge transfer reactions similar to graphite, and this charge transfer when large enough can be monitored by Raman scattering. Even when very weak charge transfer, or just gas collisions with tube walls occurs, electrical transport (resistivity and thermopower) is found to be a very sensitive probe of the perturbation on the nanotube. We first review the effects on the physical properties with reagents that produce large amounts of charge transfer (e.g., alkali metals and iodine), then move to results on gases suspected of weak charge transfer reactions with SWNT (i.e., NH3) and then finally to weaker perturbations caused by physisorbed gases, such as CO. Finally, the surprizingly strong effects on the resistivity and thermoelectric power from collisions of inert gas molecules (e.g., He) with the SWNT walls will be presented. @FootnoteText@@footnote 1@Work supported by the ONR and NSF.

10:00am **NM+NS-TuM6 Time-Resolved Diagnostic Investigations of Carbon Nanotube Synthesis***, **D.B. Geohegan**, A.A. Puretzky, X. Fan, M.A. Guillorn, D.C. Joy, M.L. Simpson, V.I. Merkulov, S.J. Pennycook,* Oak Ridge National Laboratory

Time-resolved imaging and spectroscopy measurements are applied in conjunction with ex situ TEM and FESEM investigations to understand the growth rate and mechanisms of carbon nanotube growth during laser vaporization synthesis inside a hot oven. Condensation times of atomic and molecular species in the plume are estimated using population densities of ground state species as measured by laser-induced fluorescence. Rayleigh scattering, induced blackbody emission, and real-time video techniques are used to measure the dynamics and annealing time of these condensed aggregates of clusters, nanoparticles, and nanotubes as they propagate inside the oven. By varying the growth time with these diagnostics, we have explored the rate and mechanism of single-wall carbon nanotube growth by laser vaporization through the use of high-resolution transmission electron microscopy and field emission scanning electron microscopy of deposits collected for various growth times. Z-contrast STEM combined with EELS is used to investigate the effects of size and composition of metal catalyst nanoparticles through the ability to compositionally profile individual catalyst nanoparticles. FESEM imaging in bright and backscatter modes is also used to provide a three-dimensional perspective of nanotube growth. We conclude that nanotube growth during the laser vaporization process occurs over seconds of time by the condensed phase conversion of nanoparticle feedstock by the metal catalyst nanoparticles. Ex situ annealing experiments of incompletely-converted, short nanotube 'seeds' are described which show that nanotube growth can occur outside the hot oven, supporting the condensed phase conversion growth mechanism. The possibility of varying the growth conditions to enable economically viable scale-up of nanotubes by this technique will be discussed. Research sponsored by the Laboratory Directed Research and Development program at Oak Ridge National Laboratory.

10:20am **NM+NS-TuM7 Growth of Well-Aligned Carbon Nanotubes on Nickel by Hot-Filament-Assisted DC Plasma Chemical Vapor Deposition in a CH@sub 4@/H@sub 2@ Plasma***, **Y. Hayashi**, T. Negishi, S. Nishino,* Kyoto Institute of Technology, Japan

Carbon nanotubes are expected for the electron emitters of a field emitter display (FED). In order to realize the FED, a growth method of carbon nanotubes perpendicularly well-aligned on a large-area substrate has to be developed. Recently it was reported that such aligned carbon nanotubes were grown on nickel by plasma-enhanced hot filament chemical vapor deposition (CVD) and microwave plasma CVD. We have succeeded to grow well-aligned carbon nanotubes in the area of 4 cm in diameter by hot-filament-assisted DC plasma (HF-DCP) CVD in the gas of CH@sub 4@/H@sub 2@. The growth method and conditions were as follows. DC voltage of -250V was applied to substrates relative to hot filaments. A luminous region was observed just above the substrates. By the optical emission spectroscopy, it was confirmed that the luminescence was derived from excited hydrogen and hydrocarbon radicals. Therefore the process is called HF-DCP CVD. Nickel substrates were heated by the filaments around 600 °C. The substrates were pretreated in pure hydrogen plasma for 15 min before the growth of carbon nanotubes in 20% CH@sub 4@/H@sub 2@ for 15 min. Well-aligned carbon nanotubes about 100 nm in diameter and about 5 microns in length were observed by scanning electron microscopy in the density of about 10@super 9@ cm@super -2@ on the surface of the treated specimens. Positive ions of hydrogen, carbon and hydrocarbon are accelerated in the plasma sheath toward substrates. The sheath region of DC plasma plays important roles in the growth, while hot filaments assist the maintenance of DC plasma under such low voltage. By this method, the large-area growth of well-aligned carbon nanotubes is expected.

10:40am **NM+NS-TuM8 Modeling of HiPco Process for Carbon Nanotube Production***, **T. Gokcen**, C.E. Dateo,* Eloret Corporation, NASA Ames Research Center*; M. Meyyappan,* NASA Ames Research Center*; D.T. Colbert, K.A. Smith, R.E. Smalley,* CNST, Rice University

High-pressure carbon monoxide (HiPco) reactor, developed at Rice University, is used to produce single-walled carbon nanotubes (SWNT) from gas-phase reactions of iron carbonyl and nickel carbonyl in carbon monoxide at high pressures (10 - 100 atm). Comput ational modeling is used to better understand the HiPco process. In the present model, decomposition of the precursor, metal cluster formation and growth, and carbon nanotube growth are addressed. Decomposition of precursor molecules is necessary to init i ate metal cluster formation. The metal clusters serve as catalysts for carbon nanotube growth. Diameter of metal clusters and number of atoms in these clusters are some of the essential information for predicting carbon nanotube formation and growth, which is then modeled by Boudouard reaction (2CO ---> C(s) + CO2) with metal catalysts. The growth kinetic model is integrated with a two-dimensional axisymmetric reactor flow model to predict reactor performance.

11:00am **NM+NS-TuM9 A Gas-Phase Method for Large-scale Production of Carbon Single-walled Nanotubes***, **M.J. Bronikowski**, R.K. Bradley, P.A. Willis, D.T. Colbert, K.A. Smith, R.E. Smalley,* Rice University

We have demonstrated large-scale production of high-purity carbon single-walled nanotubes (SWNT) using a gas-phase CVD process we call the HiPCO process. SWNT grow in high-pressure (10 - 100 atm), high-temperature (700 - 1200 °C) flowing CO, on clusters of catalytic metals such as iron and nickel. The metal clusters are formed in situ: metal is added to the gas flow in the form of organometallic compounds such as Fe(CO)@sub 5@ and Ni(CO)@sub 4@. Upon heating, the organometallics decompose and the metal atoms condense into clusters of 10 - 100 atoms. These clusters serve as catalytic particles upon which SWNT nucleate and grow (in gas phase) via CO disproportionation: CO + CO -> CO@sub 2@ + C(SWNT). SWNT material of up to 99 mole-% purity has been produced at rates of up to 350 mg/hr. The dependence of the quantity and quality of SWNT material produced on parameters such as temperature, pressure, catalyst concentration, catalyst composition and the presence of various catalyst enhancers (e.g., hydrogen and sulfur) will be discussed. The HiPCO process is currently being optimized and scaled for bulk production of 10 - 100 grams/day of high-purity SWNT material.

11:20am **NM+NS-TuM10 Diameter Selective Laser Ablation Synthesis of SWNTs: from 0.8 to 1.8 nm***, **M. Kappes**,* Universitaet Karlsruhe and Forschungszentrum Karlsruhe, Germany*; S. Lebedkin,* Forschungszentrum Karlsruhe, Germany

Two-pulse Laser ablation of carbon/catalyst composite rods comprising a variety of different metal combinations has been used to generate single-walled carbon nanotubes of widely varied diameter distribution. Resulting SWNTs have been characterized by (n)IR absorption and Raman spectroscopy as well as by dynamic light scattering, SEM and NMR.

11:40am **NM+NS-TuM11 Initial Growth Study of Well-aligned Carbon Nanotubes on Fe-coated Silicon Substrate by MWCVD Process***, **C.-Y. Wen**,* National Taiwan University*; L.C. Chen,* National Taiwan University, Taiwan*; C.S. Shen, Y.F. Chen,* National Taiwan University*; K.H. Chen,* Institute of Atomic and Molecular Sciences, Taiwan

Synthesis of well-aligned carbon nanotubes (CNTs) on a large area unveils the possibility to explore their properties and applications. Many synthesis methods have been reported for the growth of CNTs. Generally, it is relatively easy to generate aligned CNTs by the CVD processes. In our study, well-aligned multi-walled CNTs have been synthesized on 70 Å iron-coated silicon substrate by microwave plasma enhanced chemical vapor deposition process, wherein methane was used as carbon source. To further investigate the growth mechanism, we adopted ex-situ microscopic observation of the CNTs grown in very short growth time of several seconds. The high-resolution SEM image shows that clusters formed at the very initial stage. As the growth time extended to 40 seconds, the back-scattering image shows that metal particles were present at the tips of CNTs while metal cones appeared in the root of CNTs. After careful Ar ion beam thinning, CNTs specimens without contamination were analyzed by high-resolution TEM. The HRTEM image indicates that the clusters were precipitated iron particles of about 10 nm in diameter and graphene layers surrounded each of them. The iron precipitation continued to form cones and part of the iron was separated and encapsulated at the tip of CNTs. The growth mechanism of CNTs could be proposed from these microscopic observations. We attempt to postulate the growth kinetics of CNTs and diffusion paths of carbon species and the catalyst iron.

Processing at the Nanoscale/NANO 6
Room 302 - Session NS+NANO6+MM-TuM

Nanomechanics

Moderator: W.N. Unertl, University of Maine

8:20am **NS+NANO6+MM-TuM1 Nanomechanical Properties of Molecular Organic Thin Films***, J. Caro,* Institut de Ciencia de Materials de Barcelona (CSIC), Spain*; P. Gorostiza, F. Sanz,* Universitat de Barcelona, Spain*; **J. Fraxedas**,* Institut de Ciencia de Materials de Barcelona (CSIC), Spain

Using Atomic Force Microscopy we have studied the nanomechanical response to nanoindentations of surfaces of highly-oriented molecular organic (MO) thin films (thickness < 1000 nm). Fundamental parameters as the Young' s modulus E, unknown for most MO materials, can be estimated from the elastic deformation using Hertzian mechanics. In the case of the quasi-one-dimensional MO conductor tetrathiafulvalene tetracyanoquinodimethane (TTF-TCNQ) we obtain E ~ 22 GPa, in excellent agreement with previous reported values obtained on single crystals using neutron scattering (E ~ 20 GPa).@footnote 1@ Above ~ 200 nN the surface deforms plastically as evidenced by discrete discontinuities in the indentation curves (~ 1 nm) associated to molecular layers being expelled by the penetrating tip. The estimated critical shear stress @tau@ is ~ 2 GPa. Nanoindentation permits the determination of nanomechanical parameters of MO metastable polymorphs. This is illustrated with the MO radical p-nitrophenyl nitronyl nitroxide (p-NPNN). The @alpha@-phase of p-NPNN, stabilized as thin film,@footnote 2@ exhibits values of E and @tau@ two times smaller than the corresponding values of the thermodynamically most stable @beta@-phase. Measurements were performed with the same tip under the same experimental conditions, thus eliminating the uncertainty associated to the cantilever constant and tip radius. @FootnoteText@@footnote 1@J. P. Pouget et al. Phys. Rev. B 19 (1979) 1792. @footnote 2@J. Fraxedas et al. Europhys. Lett. 48 (1999) 461.

8:40am **NS+NANO6+MM-TuM2 Quantitative Imaging of Dynamic Mechanical Properties by Hybrid Nanoindentation***, **S.A.S. Asif**,* University of Florida*; K.J. Wahl, R.J. Colton,* Naval Research Laboratory

In this paper, we present a novel quantitative stiffness imaging technique and demonstrate its use to directly map the mechanical properties of materials with nm-scale lateral resolution. This is a powerful new approach that can eliminate tedious point-by-point analyses of indentation arrays to obtain quantitative mechanical properties of surfaces. For the experiments, we use a 'hybrid' nanoindenter, coupling depth-sensing nanoindentation with AFM scanning capabilities. AC force modulation electronics have been added, enhancing instrument sensitivity and enabling measurements of time dependent materials properties (e.g. loss modulus and damping coefficient) not readily obtained with DC techniques. Tip-sample interaction stiffness images are acquired by superimposing a small AC force (10's of nN) onto the DC imaging force (1-2 µN), and recording the AC displacement amplitude and phase as the surface is scanned. Combining a dynamic model of the indenter (having known mass, damping coefficient, spring stiffness, resonance frequency and modulation frequency) with the AC response of the tip-surface interaction allows evaluation of complex stiffness maps. We will demonstrate the use of this approach to obtain quantitative loss and storage stiffness images for elastic and viscoelastic surfaces, as well as discuss a method to directly determine loss and storage moduli from the images.

9:00am **NS+NANO6+MM-TuM3 Force-Modulated Nanoindentation of Fluorinated Polymer Thin Films Grown by PECVD***, S.A.S. Asif,* University of Florida*; E.J. Winder, K.K. Gleason,* Massachusetts Institute of Technology*; **K.J. Wahl**,* Naval Research Laboratory

Thin polymer films have been of considerable interest recently in applications for electronics packaging, solid lubrication, MEMS devices, antifouling and adhesives. However, evaluating the mechanical properties of polymer thin films is difficult due to the low elastic moduli and viscoelastic behavior typically observed with polymers. In this paper, we present an approach for measuring the mechanical and dissipative properties of thin, compliant polymer films using AC force-modulated nanoindentation.@footnote 1@ The dynamic response of the indenter is monitored during tip-sample approach, enabling sensitive detection of the surface. Adhesive interactions, contact stiffness and damping are monitored during force-displacement measurements, and hardness and modulus evaluated. In this study, we apply the above approach to investigate the correlation between polymer thin film deposition conditions and the resulting mechanical properties. The thin polymer films were deposited on Si wafers using pulsed plasma-enhanced chemical vapor deposition (PECVD). Two different source gases were used, HFPO (hexafluoropropylene oxide) and HFC-134 (1,1,2,2, tetrafluoroethane); growth conditions were varied by altering the plasma duty cycle during deposition (plasma on-time/plasma off-time). Film thickness was measured by ellipsometry and profilometry, and chemistry examined by XPS and FTIR. Film thickness varied between 100 and 400 nm. Hardness of the films varied between 0.04 to 0.2 GPa, and complex modulus between 2 and 20 GPa, with considerable damping losses observed. Comparisons between the film deposition conditions and resulting chemistry and mechanical properties will be presented and discussed. @FootnoteText@ @footnote 1@ S.A.S. Asif, K.J. Wahl, and R.J. Colton, Rev. Sci. Instrum. 70 (1999) 2408.

9:20am **NS+NANO6+MM-TuM4 Dynamic Contacts to Adhesive Viscoelastic Materials***, **M. Giri**, W.N. Unertl,* University of Maine

Dynamic mechanical contacts with nanometer to micrometer dimensions are important in scanned probe microscopy, ultra-low load indentation, microelectromechanical systems, compact discs, etc. These contacts are poorly understood if they involve adhesive viscoelastic materials such as polymers. We have studied contacts to styrene-butadiene latex films with Tg in the range 253-301 K. Contact times were in the range 0.01-1000 s and loads were up to 1 mN. Nanoindentation was used, rather than scanned force microscopy, because of its well-defined geometry and capability to control the applied load while simultaneously measuring the displacement. Diamond probes with Berkovich and spherical end shapes were used. Load vs. displacement data showed substantial adhesion hysteresis between the loading and unloading portions. The hysteresis is at least partially due to creep as indicated by the continued increase in penetration after the start of unloading. Works of adhesion were estimated by extrapolating the measured pull-off forces to long times as suggested by Johnson.@footnote 1@ Theoretical models that include adhesion but neglect long-range creep effects could not fit the data over an entire loading-unloading cycle. Creep tests were carried out under constant load. The model of Hui, Baney, and Kramer (HBK),@footnote 2@ which predicts the response of an adhesive viscoelastic contact under increasing load, was used to extract a Mode I stress intensity functional. When this functional is normalized by the indentation strain rate, it has a simple universal time-dependence. This result supports the suggestion of HBK that the stress intensity functional may be a simpler alternative to surface energy for characterization of adhesion of viscoelastic materials. @FootnoteText@ @footnote 1@K.L. Johnson in Microstructure and Tribology of Polymers,Eds. V.V. Tsukruk and K.J. Wahl (ACS Books, 2000). @footnote 2@C.Y. Hui, J.M. Baney, E.J. Kramer, Langmuir 14 (1998) 6570.

9:40am **NS+NANO6+MM-TuM5 Precision Nanoscale Machining with STM-QCM***, **J. Krim**, B. Borovsky,* North Carolina State University

We have constructed an apparatus which allows us to investigate the nanoscale machining of metal surfaces resulting from the contact of a sharp tip with a high speed vibrating surface (maximum speeds over 1 m/s).@footnote 1@ The tip (tungsten or platinum alloy) is that of a Scanning Tunneling Microscope (STM), and the surface is that of a metal film deposited onto a Quartz Crystal Microbalance (QCM). The STM-QCM combination enables machining-and-imaging experiments in which the topography of the substrate is compared before, during, and after tip-surface rubbing contact at well-defined locations. The rubbing contact is either direct tip-surface contact or tunneling contact through an oxide layer. While the STM tip alone is able to machine softer materials (such as copper), the high speed vibrations of the QCM greatly enhance machining of more durable materials and oxide films. Specially prepared surfaces permit the creation of sharper, more detailed structures with 10 to 100 nm dimensions, as is demonstrated using copper and silver surfaces exposed to oxygen gas. Our talk focuses on the robustness of resulting structures compared to the ease with which they were machined. Research supported by the NSF and the AFOSR. @FootnoteText@ @footnote 1@ B. Borovsky, B. Mason, and J. Krim, submitted to J. Appl. Phys.

10:00am **NS+NANO6+MM-TuM6 Size-Dependent Mechanical Properties of MoO@sub 3@ Nanoplates***, **J. Wang**, K.C. Rose, J.W. Hutchinson, C.M. Lieber,* Harvard University

The mechanical properties of materials on the nanometer scale are of great interest both for furthering our fundamental understanding as well as for use in a wide range of micro- and nano-mechanical systems. Previous experimental studies have focused on one-dimensional systems, including carbide nanorods and carbon nanotubes. For example, atomic force microscopy (AFM) has been used to show that silicon carbide nanorods have similar Young's moduli to defect free macroscopic crystals and that carbon nanotubes are much stiffer than carbon whiskers and fibers. Here, we used AFM to determine the bending stiffness of individual, structurally-isolated molybdenum oxide (MoO@sub 3@) nanocrystal nanoplates (5-16 nm thick). These nanoplates were pinned to molybdenum disulfide (MoS@sub 2@) surfaces on one side and were suspended freely over MoS@sub 2@ steps on the other side. Bending forces were measured versus displacement on the unpinned side of these MoO@sub 3@ nanoplates. Finite element analysis revealed that the effective Young's moduli of these MoO@sub 3@ nanocrystals are significantly smaller than that of bulk MoO@sub 3@ single crystals and that the moduli decrease with decreasing nanocrystal thickness. This novel behavior was further substantiated in subsequent experiments where it was shown that MoO@sub 3@ nanocrystals (1.4 - 5 nm thick) had enormous flexibility when slid over multilayer MoS@sub 2@ steps. These results have important implications for the sliding of nanoscale structures on rough surfaces and even for the fabrication and manipulation of smaller mechanical systems evolving in nanotechnology.

10:20am **NS+NANO6+MM-TuM7 High Frequency Nanomechanical Systems***, **D.W. Carr**,* Lucent*; L. Sekaric, A. Olkhovets, S. Evoy, J.M. Parpia, H.G. Craighead,* Cornell University **INVITED**

Nanofabricated mechanical systems are highly useful tools for research in physics, optics, and dynamics. We have developed fabrication processes that allow us to make suspended nanostructures in silicon and silicon nitride. We can actuate motion in these structures using electrostatic forces, and this motion is detected optically using interferometric effects. This measurement technique is sensitive to sub-nanometer motion. We have measured doubly-clamped silicon beams with fundamental resonant frequencies as high as 380 MHz. Such structures are being considered for use as chemical and biological sensors, force gauges and frequency filters. One of the obstacles for practical applications are intrinsic losses which lower the mechanical quality factor (Q-factor) of these devices. We see a strong dependence in the Q-factor on the width of these beams. As the width decreases below 100 nm, the Q factor drops sharply, indicating that the dominant energy loss mechanisms are surface related. We are also focusing on surface treatment and the effects of device geometry on dissipation. We have conducted a study of the effects of amorphous metal layers that are used in driving and detection schemes for NEMS and found that the metal layers have a detrimental impact on the devices' mechanical quality factor. We are also studying the effects of various levels of doping in single-crystal silicon on dissipation and driving schemes, a study significant for industrial use in integration with electronic devices. We have also studied the effect of parametric amplification in very small torsional resonators. An applied bias voltage effectively changes the spring constant of the system. Oscillating this bias at a specific frequency results in an amplification of the resonant motion. Swept-frequency measurements show interesting properties of the resonant spectrum, and these results agree well with the theory. Such systems may have interesting application in resonant sensors and surface probes.

11:00am **NS+NANO6+MM-TuM9 Quantum Well Micromechanical Photon Detectors***, **P.G. Datskos**, S. Rajic, L.R. Senesac,* Oak Ridge National Laboratory*; I. Datskou,* Environmental Engineering Group, Inc.

We have developed a method of fabricating quantum well microstructure arrays for a variety of sensing applications. Microstructures with quantum wells allow real-time manipulation of energy states using external stress. For example this can result in an effective and rapid change in electron energy levels in photon detection devices. Such changes make possible tuning the levels to respond to desired wavelengths. We applied such GaAs/GaAlAs micromechanical quantum well arrays to detection of photons and especially uncooled infrared detection. We will present and discuss our results.

11:20am **NS+NANO6+MM-TuM10 Nanomechanical Systems***, **M.L. Roukes**[1],* California Institute of Technology **INVITED**

Microelectronics technology is now pushing deep into the submicron regime, yet, for the most part, work on micromachines still remains back at the few micron scale, or larger. The time is ripe to embark upon a concerted exploration of mechanical systems at the nanoscale. In this talk will highlight the promise and intrigue of this domain. Nanoelectromechanical systems, or NEMS, are MEMS scaled to submicron dimensions. In this size regime, it is possible to attain extremely high fundamental frequencies while simultaneously preserving very high mechanical responsivity (small force constants). This powerful combination of attributes translates directly into high force sensitivity, operability at

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[1] **Featured Speaker - Science and Technology in the 21st Century**

ultralow power, and the ability to induce usable nonlinearity with very modest control forces. In this overview, I shall provide an introduction to NEMS and will outline several of their exciting initial applications. Our recent efforts at Caltech have culminated in nanomechanical devices with potential for new applications in electronics and metrology. These include development of the first VHF (very high frequency) mechanical resonators;@footnote 1@ the development of mechanical electrometers yielding sensitivity below a single electron charge;@footnote 2@ explorations of thermal transport and energy equilibration in nanoscale devices,@footnote 3@ which have recently culminated in the measurement of the quantum of thermal conductance;@footnote 4@ and development of mechanically-detected magnetic resonance imaging.@footnote 5@ However, a rather stiff entry fee exists at the threshold to this new domain, new engineering is crucial to realizing the full potential of NEMS. Our work also serves to indicate some of the most crucial issues that must be addressed before the full potential of nanomechanical systems can be realized. An important example is that certain mainstays in the methodology of MEMS will, simply, not scale usefully into the regime of NEMS. Most problematic among these issues are the size of the devices compared to their embedding circuitry, their extreme surface-to-volume ratios, and their unconventional "characteristic range of operation". These give rise to some of the principal challenges in developing NEMS. Prominent among these are the need for: ultrasensitive, very high bandwidth displacement transducers; an unprecedented control of surface quality and adsorbates; novel modes of efficient actuation at the nanoscale; and precise, yet robust and reproducible approaches to surface and bulk nanomachining. Ultimately nanomechanical devices will permit access to a regime where mechanics is determined by atomistic properties; where quantum, rather than thermal, fluctuations predominate; where force and displacement detection can meet, or even exceed, the standard quantum limit; and where thermalization involves "granular" heat flow via individual phonons.@footnote 6@ I will conclude by making some projections about this domain that initially seems exotic, but is, in reality, imminent. @FootnoteText@ @footnote 1@ A.N. Cleland and M.L. Roukes, "Fabrication of High Frequency Nanometer Scale Mechanical Resonators from Bulk Si Substrates", Appl. Phys. Lett., 69, 2653 (1996). @footnote 2@ A.N. Cleland and M.L. Roukes, "A Nanometre-Scale Mechanical Electrometer", Nature 392, 160 (1998). @footnote 3@ T.S. Tighe, J.M. Worlock, and M.L. Roukes, "Direct Thermal Conductance Measurements on Suspended Monocrystalline Nanosturctures", Appl. Phys. Lett. 71, 2678 (1997). @footnote 4@ K. Schwab, E.A. Henriksen, J.M. Worlock, and M.L. Roukes, "Measurement of the Quantum of Thermal Conductance", Nature 404, 974 (2000). @footnote 5@ P.C. Hammel, Z. Zhang, G.J. Moore, and M.L. Roukes, "Subsurface Imaging with the Magnetic Resonance Force Microscope", J. Low Temp. Phys. 101, 59 (1995). / P.C. Hammel, Z. Zhang, M.Midzor, M.L. Roukes, P.E. Wigen and J.R. Childress, "The Magnetic Resonance Force Microscope", in "Frontiers in Magnetism of Reduced Dimensional Systems", B.G. Bar'yakhtar et al., eds., (Kluwer Academic, 1998). @footnote 5@ M.L. Roukes, "Yoctocalorimetry: Phonon Counting in Nanostructures", Physica B: Condensed Matter 263-264, 1 (1999).

Photonics

Room 310 - Session PH-TuM

Fundamental Properties and Applications of Photonic Materials

Moderator: K. H. A. Bogart, Bell Laboratories, Lucent Technologies

8:20am **PH-TuM1 Integrated Photonics for Optical Communications: A Materials Processing Challenge***, A.E. White,* Bell Laboratories, Lucent Technologies **INVITED**

The drive to higher and higher lightwave transmission capacity has come in part through deregulation, but also from demand for internet access, telecommuting, and broadband services. Historically, in order to meet that demand, service providers used higher transmission rates, but now there is a clear trend toward wavelength division multiplexing (WDM), which has some significant advantages. When the switching is done in the optical layer, it will be possible to have true wavelength routing and a reconfigurable network. To implement this vision, a number of sophisticated optical components will be required. In the late 1980's, researchers started to explore whether the functionality of passive optical components, such as fibers and taps, could be combined, similar to the way that electrical components (resistors, capacitors, and transistors) are combined in an integrated circuit (IC). The primary goal was to reduce manufacturing costs, but the additional advantages of ICs, such as reduced size, increased performance (especially at high speeds), and greater reliability, are also be desirable in photonics. The silicon wafer can be used as a platform to attach lasers and detectors as well, hence the name "silicon optical bench" for this technology. Silicon optical bench technology leverages off the silicon IC industry for low cost, high quality flat substrates as well as processing developments and equipment. Initially, the focus was on passive waveguide structures and considerable effort went into designing a materials and processing technology that would be compatible with standard semiconductor manufacturing equipment and would also produce planar waveguides that were well-matched to standard single mode (SM) optical fiber. As the devices become more complex - from routers, to reconfigurable add/drop filters, to Er-doped planar waveguide amplifiers - new materials and processing challenges have arisen.

9:00am **PH-TuM3 Infrared Ellipsometry Characterization of Porous Silicon Bragg Reflectors***, S. Zangooie, M. Schubert, C. Trimble, D.W. Thompson,* ***J.A. Woollam,*** University of Nebraska, Lincoln

Porous silicon (PS) has been the subject of intensive investigation for applications of the material in disciplines such as silicon based electronics, gas- and biosensor technologies, as well as optics. Industrial applications of PS demand fast and non-destructive determination of the material properties in terms of, e.g., thickness, porosity and surface chemical characteristics. In this work variable angle of incidence infrared spectroscopic ellipsometry is employed to simultaneously determine the real and imaginary parts of the dielectric function of the solid phase of the porous silicon Bragg reflectors without the necessity for additional measurements on reference samples, employment of the Kramers-Kronig technique, or extrapolation of experimental data beyond the measurement range. In addition to the thickness, volume porosity, inhomogeneity and optical anisotropy, properties of the solid part of the porous material are investigated in terms of the optical dielectric function and surface chemistry. The high sensitivity of the technique is employed to detect and identify infrared resonant absorptions related to different Si-H as well as Si-O-Si vibrational modes. Resonances due to Si@sub 2@-Si-H@sub 2@, Si@sub 3@-Si-H, Si@sub 2@-Si-H@sub 2@, Si-O-Si stretching modes, as well as Si@sub 2@-Si-H@sub 2@ scissor and Si@sub 2@-Si-H@sub 2@ wagging mode are revealed and characterized. A relatively large resonance at 626 cm@super -1@ is attributed to the Si-Si bond stretching caused by the asymmetry in surface related bonds creating an IR-active net dipole moment. The material is found to have positive birefringence. The electrical resistivity of the solid part of the porous material is determined to be 0.03 @ohm@ cm, and larger than the corresponding bulk value of 0.019 @ohm@ cm. Furthermore, the carrier concentration in the investigated porous material shows a decrease from 6.2 * 10@super 18@ cm@super -3@ to 4 * 10@super 18@ cm@super -3@.

9:20am **PH-TuM4 IR Fiber Optics Development at the Naval Research Laboratory***,* ***J.S. Sanghera,*** Naval Research Laboratory **INVITED**

IR transmitting chalcogenide glasses and fibers are being developed at the Naval Research Laboratory for numerous military, commercial and biomedical applications in the infrared region. Significant progress has been made in the areas of chemical and glass purification, glass fabrication and fiberization technology. Consequently, long lengths of optical fibers have been fabricated that possess low loss, high strength and high threshold to laser damage. The fibers are being developed for, and implemented in, infrared countermeasure systems, threat warning systems and fiber optic based chemical sensor systems for facility clean up and environmental monitoring as well as biomedical tissue diagnostics. The fibers have also been used in a scanning near field infrared microscope (SNIM) to demonstrate an optical resolution of 100 nm and topographic resolution of 20 nm. The ability to dope these materials with rare earth ions has led to bright sources in the IR beyond 2 um which are useful for characterizing missile seekers and focal plane array detectors. In addition, these low phonon energy glasses are excellent hosts for rare earth ions for making potential lasers and amplifiers. We will present our latest results regarding fabrication of the fibers, fiber properties and their applications.

10:00am **PH-TuM6 First-Principles Study of Oxygen-Deficient Defects in Silicate and Germanosilicate Glasses***, K. Raghavachari,* Bell Laboratories, Lucent Technologies

The prominent 5-eV absorption band in silicate and germanosilicate glasses has been the subject of extensive investigations by many groups. Several defect models involving oxygen deficiency have been proposed to explain the experimental observations. In particular, careful analysis of the associated photoluminescence bands indicates the presence of more than one component to the absorption band. However, the microscopic defect models responsible for this absorption band are still under debate. In this work, we have investigated the structural and electronic properties of oxygen deficient defects in silicate and germanosilicate glasses by first-principles quantum chemical studies using a cluster approach. In particular, the photoabsorption and photoluminescence properties of several competing defect models have been evaluated. The performance of different quantum chemical methods for the accurate calculation of the optical properties of defects is assessed. The effect of Ge on the relative thermodynamic stabilities of the defects is examined. Careful comparisons are performed with the known experimental observations. New models are proposed to explain the different components of the 5-eV photoabsorption band in glasses.

10:20am **PH-TuM7 Dynamic Polymeric Photonic Components***, **L. Eldada,*** Telephotonics, Inc. **INVITED**

A key advantage of polymeric materials over more conventional optical materials such as glass, is the considerably larger variation that their refractive index undergoes with temperature. The large magnitude of the thermo-optic coefficient dn/dT (about 25 times larger in most polymers than in glass) can be leveraged to produce power-efficient thermally actuated dynamic photonic components. We review the global advances in thermo-optic polymeric components which include switches, tunable filters, and variable optical attenuators (VOA's). NxN switches can be digital optical switches based on X junctions or Y junctions, or they can be interferometric switches based on directional couplers or Mach-Zehnder interferometers (MZI's), including generalized MZI's (GMZI's) which are compact devices that consist of a pair of cascaded NxN multimode interference (MMI) couplers with thermal phase shifters on the N connecting arms; tunable filters can be based on phasars, gratings, thin films, or microring resonators; and VOA's can be based on interferometry, mode confinement, or switching principles.

11:00am **PH-TuM9 The Understanding and Realization of Photonic Crystals***, **C.A. White,*** Bell Laboratories, Lucent Technologies **INVITED**

Interest in photonic crystals has shown explosive growth in recent years. This interest spawns from the potential for new devices ranging from new optical crossconnects to novel lasers to microstructured optical fiber as well as the possibility of experiments in fundamental physics ranging from enhanced fluorescence lifetimes to atomic traps. All of these applications are made possible not because of the discovery of new physical phenomena, rather through a novel manner of looking at conventional optics. In this talk, I will discuss the theory of these new materials highlighting how relatively simple optical concepts give rise to the exciting properties photonic crystals. I will construct a simple intuitive notion of what defines a photonic crystal and specifically what gives rise to the photonic band gap. Building on this discussion of the physics, I will present our efforts on the realization of two and three dimensional photonic crystals at Bell Laboratories.

11:40am **PH-TuM11 Plasmonics: Electromagnetic Energy Transfer and Switching Below the Diffraction Limit in Nanoparticle Chain Arrays***, **M.L. Brongersma,*** California Institute of Technology, US*; S.A. Maier, H.A. Atwater,* California Institute of Technology

The integration density of integrated optics appears to face the fundamental limitation that structures for guiding and modulation of light must have dimensions comparable to the wavelength of light. Recently however, it was theoretically shown that this problem can be circumvented by "plasmonics", i.e., transport of electromagnetic energy along linear chains of closely spaced 10-50 nm diameter metal nanoparticles. This transport relies on the coupled near-field electrodynamic interaction between metal particles that sets up coupled plasmon modes. We have modeled the electromagnetic transport properties of corners, tees, and switches that consist of chains of metal nanoparticles. Both full electromagnetic field calculations using finite difference time domain methods and calculations in the point dipole approximation indicate strong guiding of electromagnetic radiation, and electromagnetic dispersion relations are obtained. It is shown that propagation is coherent and the group velocities can exceed saturated velocities of electrons in semiconductors (about 10^5 m/s). High efficiency transmission of energy around sharp corners is possible. The transmission is a strong function of the frequency and polarization direction of the plasmon mode. The factors dictating the choices for particle and host material will be described. To date, we have also performed experiments using nanophotonic analog structures that operate in the microwave frequency regime. We find that in analogs to optical plasmonic devices operating at 8 GHz, the transmitted intensities around both sharp corners and tees are high and closely agree with the results of microwave device simulations. Finally, the operation of a "plasmon switch" that acts as an all-optical inverter is modeled. Recent efforts to fabricate and test nanoscale plasmonic structures will be discussed; we note that such "plasmonic devices" potentially are among the smallest structures with optical functionality.

Plasma Science and Technology
Room 311 - Session PS-TuM

Modeling of Plasma Processes

Moderator: D.J. Economou, University of Houston

8:20am **PS-TuM1 Optimization of Plasma Processing for Manufacturing Using Fast Integrated Models***, B.Y. Yu, T.P. Phung,* ***S.S. Shankar,*** Intel Corporation

Plasma processes are widely used in semiconductor manufacturing and a better understanding of the underpinning plasma and chemical principles is essential for better equipment design and process control. The major problems encountered in the plasma reactor are the non-uniformity at the wafer-level, etch profile controllability, and contamination. A fast and physically based integrated simulation tool has been developed to provide validated simulations of plasma processes, chemical reactions, transport, and surface evolution. The tool is employed to aid in understanding the plasma etching as a function of equipment variables. The tool consists of (1) a three-dimensional multi-species transient plasma processing simulator with capabilities for predicting wafer-level etch rate and uniformity, (2) a feature-level model for surface topographic evolution, and (3) a multi-scale linker to self consistently connect physical quantities between the two length scales@footnote 1,2@ In addition, different advanced numerical techniques have been developed for simulating realistic systems with multiple gas and surface chemistry. The plasma simulator is demonstrated on unstructured three dimensional grids with transport of mass, momentum, and energy. We have employed the integrated simulator to study multiple process windows in two different processes such as plasma physical sputtering of oxide (inter-layer dielectric) and CF4-based oxide etching. Simulation results are compared with experiments. @FootnoteText@ @footnote 1@ S.T. Rodgers, K.F. Jensen, J of App. Phys, (1997) @footnote 2@ S.T. Rodgers, S. Shankar, U. Hansen, and K.F. Jensen, J of Appl. Phys (submitted, 1999)

8:40am **PS-TuM2 Modeling Transport and Etch Chemistry in High Density Plasmas***, **M.W. Kiehlbauch**, D.B. Graves,* University of California, Berkeley

In high density plasmas there is a complex interplay between neutral transport, charged particle transport, and gas and surface chemistry. High rates of mass, momentum and energy plasma/neutral collisional interchanges lead to large neutral gradients. Additionally, the low flow rates of these systems combined with fast diffusion and surface reaction often lead to species velocities that are much larger than the overall convective velocity. This makes for a difficult numerical problem that requires a self-consistent treatment of non-Fickian diffusion, chemistry, neutral convection, and plasma/neutral collisions. A two-dimensional, coupled plasma and neutral simulation has been developed and applied to high density inductively coupled plasmas used in etching high-k materials, an emerging area of semiconductor technology. Potential candidates are typically metal oxides, e.g. ZnO@sub 2@, and are etched using chlorine chemistry. Etch products often have low volatility. Neutral transport and surface reaction are especially important for low volatility species, which must be efficiently removed from the reactor before they can redeposit on the wafer or reactor walls. Failure to do so results in a build-up of reaction products and can lead to a loading effect. We present results showing that neutral transport is dominated by diffusion induced by gas or surface chemistry, depending upon the operating regime. We show that neutral transport can be a key factor in determining etch performance. Finally, simulation results will be used to suggest operating strategies that will optimize the etch process and minimize the use of consumables such as power, coolant and feedgases.

9:00am **PS-TuM3 Plasma Chemistry Model for Fluorocarbon Etching of SiO@sub 2@***, **P. Ho,** J.E. Johannes, R.J. Buss,* Sandia National Laboratories*; E. Meeks,* Reaction Design **INVITED**

Plasmas of C@sub 2@F@sub 6@, CHF@sub 3@ and other fluorocarbons are used to etch silicon dioxide layers in the fabrication of microelectronic devices. Computational modeling of these systems can accelerate the design and optimization of these commercially important processes and equipment. We have developed a detailed model of the gas-phase and surface chemistry occurring in the C@sub 2@F@sub 6@ plasma - SiO@sub 2@ system. Reaction rates were obtained from independent published cross section and chemical kinetic data, whenever possible, or are estimates based on data for related molecules. A wide variety of experimental data from several experimental reactors were used to develop and validate the chemical mechanism. We have attained good overall agreement with the set of blanket etch rates, electron densities, negative ion densities, neutral species densities (i.e. CF, CF@sub 2@ and SiF) and ion current density data available to us. The work described here is part of a larger project on plasma etching funded by SEMATECH, and the work at Sandia National Laboratories was done under CRADA No. 1082. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract DE-AC04-94AL85000.

9:40am **PS-TuM5 Sustaining Another Decade of Innovation in Plasma Equipment and Process Design: Needs and Challenges@footnote 1@**, ***M.J. Kushner***[1], University of Illinois at Urbana-Champaign **INVITED**

Plasma equipment and process design have matured from a largely empirical practice to a science based discipline during the past decade based, in part, on the improvement of our fundamental understanding of the dominant processes through application of diagnostics and modeling. Sustaining this innovation in equipment and process design through the next decade will be challenged by increasingly stringent demands for reliability, speed of development and increased functionality of tools. As the market for microelectronics trifurcates into high performance, but commodity components manufactured largely by foundries, select extreme performance silicon components, and non-silicon advanced logic and optoelectronics, the demands for equipment and process design will likely also be segmented. The role of non-traditional components, such as MEMS, adds an additional dimension of uncertainty. In this talk, the challenges which will need to be met to sustain innovation will be discussed, with emphasis on the role of diagnostics and modeling. @FootnoteText@ @footnote 1@Work supported by SRC, NSF, AMAT, LAM and DARPA/AFOSR.

10:20am **PS-TuM7 Electron Transport and Power Deposition in Magnetically Enhanced Inductively Coupled Plasmas@footnote 1@**, ***R.L. Kinder***, *M.J. Kushner,* University of Illinois at Urbana-Champaign

The ability to deposit power within the volume of the plasma in Magnetically Enhanced Inductively Coupled Plasmas (MEICP) strongly depends on the magnetic field strength and configuration. The coupling of electromagnetic fields to the plasma typically occurs through a weakly damped helicon wave that penetrates into the bulk plasma and an electrostatic wave (the TG-mode). The TG-mode may penetrate into the plasma at low magnetic fields but deposits most its power near the plasma-surface interface at high magnetic fields. Under select conditions, the phase velocity of the helicon wave is similar to the thermal velocities of electrons which enables power deposition through collisionless heating. To investigate these processes, the Hybrid Plasma Equipment Model (HPEM) was improved by including a full tensor conductivity and electrostatic source terms in solution of Maxwell's equations, and by including 3-d components of the electric field in the electron Monte Carlo Simulation to resolve electron energy distributions (EEDs). Plasma parameters, wave propagation and location of power deposition will be discussed for process relevant gases (e.g. Ar/Cl@sub 2@, Ar/CF@sub 4@) as a function of magnetic field strength, configuration, and power. In the absence of the TG mode, with increasing B-field, electric field propagation progressively follows B-field lines and significant power can be deposited downstream. The tails of the EEDs are enhanced in the downstream region indicating some amount of electron trapping. Volumetric power deposition is ultimately limited by damping of the TG mode and the helicon wavelength. Wave propagation can be suppressed in electronegative gas mixtures where the wavelength exceeds the chamber dimension. @FootnoteText@ @footnote 1@Work supported by LAM, AMAT, SRC, NSF and DARPA/AFOSR.

10:40am **PS-TuM8 Surface Reaction Model for Etch-rate Calculations in SiO@sub 2@ Selective Etching**, ***S. Kobayashi***, *T. Tatsumi, M. Matsui, K.K. Kawashima, M. Sekine,* Association of Super-Advanced Electronics Technologies (ASET), Japan

A surface reaction model was constructed to predict Si and SiO@sub 2@ etch rates in fluorocarbon plasma. This model is based on experimental results, obtained in a dual-frequency (27/0.8 MHz) parallel-plate RIE system@footnote 1@ that is widely used in manufacturing processes. Although it is not based on a first-principal calculation, we carefully tried to keep physical meanings in the calculation. At the first, we chose input parameters, such as ion energy, ion flux, incident flux of CF@sub x@ species, and oxygen atom flux measured by various in-situ diagnostics such as IRLAS, QMS, and OES. Then, the reaction probability between fluorine and Si or SiO@sub 2@, and the energy loss by a C-F polymer layer were estimated from the experimental data. Based on this model, a simulation program was coded. The calculation starts on the clear Si or SiO@sub 2@ surface. Using the parameter set such as C-F species flux, ion flux and energy, the C-F polymer thickness and the etched amount were alternately calculated because each value depends on each other. Therefore, the calculation is iteratively continued until the variation of the C-F polymer thickness becomes small enough. We performed the calculation and obtained the selectivity when varying the C@sub 4@F@sub 8@ and oxygen flow rates individually. A highly selective etch process could be predicted using the model calculation and discussed the best condition for the etching process using a calculation instead of a conventional experimental analysis. @FootnoteText@ This work was supported by NEDO. @footnote 1@T.Tatsumi et al., J. Vac. Sci. Technol., A17 (1999) 1562.

11:00am **PS-TuM9 3D Monte-Carlo Simulation of SiO@sub 2@ Film Growth Combined with Gas-phase Kinetic Model of TEOS-O@sub 2@ Plasma**, ***A. Rhallabi***, *P. Retho, A. Granier, A. Goullet, G. Turban,* IMN University of Nantes, France

A gas phase kinetic model of TEOS-O@sub 2@ plasma mixture combined with 3D Monte-Carlo surface model is developed to predict the microscopic properties of SiO@sub 2@ film as a function of the plasma parameters. The gas phase kinetic model is based on the mass balance equations of reactive species diffusing toward the surface. The mass balance equations in the diffusion chamber of our helicon reactor only take into account the electron impact dissociation and ionization rates of both TEOS and oxygen. Indeed, the low pressure (1 - 10 mTorr) and high density plasma allow to neglect the gas phase molecular reaction rates because the mean free path of the reactive species is large. In these conditions, the formation of the TEOS fragments (SiR@sub n@(OH)@sub 4-n@ where n=1-3 and R is OC@sub 2@ H@sub 5@) containing at least one OH group is mainly due to the dissociation of the R group into OH group by electron impact. On the other hand, a 3D kinetic Monte-Carlo model is developed to study the SiO@sub 2@ film growth. The fluxes of the reactive species are determined from the gas phase kinetic model. The SiO@sub 2@ growth process is mainly ensured by reaction between silicon sites and reactive precursors SiR@sub n@ (OH) @sub 4-n@ leading to the formation of oxygen bridges and the elimination of water. The nucleation phase mechanism was introduced in the surface model and showed the role of the substrate surface energy on the SiO@sub 2@ film adherence. The effects of some plasma parameters such as the RF power and the oxygen percentage on the deposition rate and the microscopic structure of the film are analyzed.

11:20am **PS-TuM10 Integrated Ionized and Conventional PVD Process Analysis Comparisons**, ***P. Ventzek***, *V. Arunachalam, S. Rauf,* Motorola Inc.

Conventional physical vapor deposition (PVD) processes or variations on them are still prevalent as tools for thin film deposition and are often the process of choice when damage or cost of ownership issues are considered. Integrated equipment feature scale models are required to facilitate making the decision whether conventional processes or their variants can do the job of the more sophisticated IPVD tools. Integrated models (equipment to feature) exist for conventional PVD processes but it is rare that the plasma physics aspects of the models are folded into the analysis. Reasons for this include that the coupling the magnetron physics into the model is not easy and that reactive sputtering processes which are more often than not conventional PVD processes are themselves complex. First, we will describe the coupling of a phenomenological magnetron model with the Hybrid Plasma Equipment Model (University of Illinois). Then, this paper will compare the performance (equipment to feature) of generic IPVD and PVD tools. Performance is quantified in terms of ion and neutral angular and energy distribution functions, fluxes of species to the wafer/feature and resultant feature profile.

11:40am **PS-TuM11 Modeling and Experimental Verification of a Ti/Nitrogen/Ar Ionized Physical Vapor Deposition Tool**, ***K. Tao***, *D. Mao, J.A. Hopwood,* Northeastern University

Ionized physical vapor deposition (IPVD) is one method used to deposit TiN barrier layers by the semiconductor industry. Compared to conventional

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physical vapor deposition or sputtering, IPVD can achieve directional deposition of thin films into high-aspect-ratio features. Metal atoms sputtered from the target are ionized by high-density plasma and the metal ions are collimated to the substrate by the electric field in the plasma sheath. Although some work has been reported on TiN film deposition by IPVD,@footnote 1@ there is little understanding of the plasma fundamentals of reactive sputter deposition using IPVD. In this work reactive IPVD is being studied both experimentally and through plasma modeling. A global model of Ti-Ar-N@sub 2@ plasma is developed to predict the densities of the main plasma species, e.g. ionized, excited and dissociated particles of Ti, Ar and nitrogen. For a given chamber length and diameter, absorbed power, total pressure and gas flow rates, the particle and energy balance equations are solved to determine the plasma species densities and the electron temperature. To verify the validity of the model we carried out plasma diagnostics that include mass spectroscopy, optical emission spectroscopy and Langmuir probes. The dissociation of nitrogen is used to benchmark the model. By altering the N surface recombination coefficient we model the transition between the "metallic" and "nitrided" target modes. Experimental data show that the surface recombination coefficient for N is nearly 100% when the target is in metal mode because the freshly deposited Ti on the chamber walls increases the N sticking ability. A comparison of the model with the measured nitrogen dissociation ratios implies that the N surface recombination coefficient decreases to approximately 25% in the nitride mode. @FootnoteText@ @footnote 1@ J. Forster, Ionized Physical Vapor Deposition, Thin Films vol. 27, 141 (Academic Press, San Diego, 2000).

Semiconductors
Room 306 - Session SC+EL+SS-TuM
Compound Semiconductors

Moderator: J.W. Rogers, Pacific Northwest National Laboratory

8:20am **SC+EL+SS-TuM1 Reconstructions and Steady-state Surface Structures on InAs(001)-(2x4): Implications for Atomistic Modeling of Growth***, **W. Barvosa-Carter**, F. Grosse,* HRL Laboratories and University of California, Los Angeles*; M. Gyure,* HRL Laboratories*; J.H.G. Owen, C. Ratsch,* HRL Laboratories and University of California, Los Angeles*; R.S. Ross, J.J. Zinck,* HRL Laboratories

Heterostructures involving InAs, GaSb, and AlSb are increasingly finding applications in high-frequency, infrared, and 'spin-tronic' devices. Interface structure in these devices can be critical in determining device performance. The robustness of any model that seeks to relate process parameters and in-situ sensor signals to the surface chemistry or roughness of the growing film ultimately depends on our understanding of the relevant surface reconstructions and epitaxial growth mechanisms. Using MBE, RHEED, and atomic-resolution STM, we have studied the reconstructions and 'steady-state' surface structures present on MBE-grown InAs homoepitaxial surfaces in the (2x4) growth regime. On InAs we find two reconstructions that are relevant for growth: the familiar @beta@2(2x4) (as on GaAs) and the less familiar @alpha@2(2x4). We find excellent agreement between detailed atomic-resolution STM and first-principles simulated images of these structures. Upon quenching, we find that "steady-state" InAs surfaces exhibit small islands and adatom-like structures residing on a disordered mixture of the @beta@2 and @alpha@2 reconstructions, and that the proportions of these structures vary as a function of As pressure and temperature. Hence, the growth surface structure for InAs is remarkably different than for GaAs, where only the @beta@2 reconstruction is present with relatively few defects under device growth conditions. These results are in excellent qualitative agreement with an ab initio-based Monte Carlo model that is being developed in parallel with the experimental effort to describe reconstructions and growth on this surface.

8:40am **SC+EL+SS-TuM2 Oscillations of Local Density of States at the Epitaxially Grown InAs(111)A Surfaces Characterized by Low-temperature Scanning Tunneling Microscopy***, **K. Kanisawa**, M.J. Butcher, H. Yamaguchi, Y. Hirayama,* NTT Basic Research Laboratories, Japan

The characterization of semiconductor surface electrons is very important for understanding microscopic electron behavior. Though the local density of states (LDOS) has been studied at metal surfaces by using low-temperature scanning tunneling microscopy (LT-STM), the only studies that have been reported for semiconductors are on cleaved (110) surfaces. A LT-STM study of an epitaxial semiconductor surface makes it possible to compare the electron behavior directly with nanometer-scale morphology. We have performed a LT-STM study of the epitaxially grown InAs(111)A surface on the GaAs(111)A substrate in layer-by-layer growth mode at 5 K. Topographic and dI/dV images were obtained simultaneously by using a lock-in technique. In the dI/dV images, LDOS oscillation patterns were clearly imaged at surface defect sites, which were identified in the corresponding STM images. At an isolated defect, clear LDOS Friedel oscillations made of concentric circles were observed. From the dependence of the oscillation period, the effective mass was calculated to be 0.043m@sub 0@, which is consistent with that of InAs with a relatively high electron concentration. In the case of steps with a height difference of integral monolayers, the oscillation patterns showed dark bands along the steps. In contrast the Frank partial dislocations, with height differences of fractional monolayers, showed bright bands. This implies that there are large differences between the electron scattering phases at the steps and at the dislocations. During the InAs growth, triangular regions are formed on the surface by three {111} stacking fault planes. Such boundaries showed symmetric and regular patterns inside. Our detailed analysis suggests that these patterns are related to zero-dimensional electron systems confined within the InAs nanostructures.

9:00am **SC+EL+SS-TuM3 Something Old, Something New, Something Borrowed, Something BLUE - Fifty Years of III-V Compound Semiconductors!***, **R.D. Dupuis**[1],* University of Texas, Austin **INVITED**

III-V compound semiconductors, first identified in 1950, have become critically important for the commercial development of advanced semiconductor devices and systems. In the past fifty-some years, many workers from all over the world have contributed to this outstanding success. The epitaxial growth of III-V films began in 1960 with the early work of Holonyak who used iodine transport in a closed tube to produce epitaxial layers of GaAs/GaAs, GaAs/Ge, and various GaAsP alloys. Open-tube VPE and LPE for III-Vs were developed soon after this work. In 1967, Manasevit, et al., demonstrated the metalorganic chemical vapor deposition (MOCVD) epitaxial growth process and in 1970 Cho, et al. reported the first molecular beam epitaxy (MBE) growth of GaAs. Thus, twenty years after the first identification of III-Vs as semiconductors, all of the epitaxial growth processes we use today had been developed. It has taken 30 more years of technological and scientific advances to arrive at the understanding of these materials that we take for granted today. In fact, much of the new advanced communications systems that will be employed in the next 10 years depend fundamentally upon III-V epitaxial growth. In this talk, I will briefly review some aspects of the history of the development of these material systems and growth processes and I will discuss some of the recent results as well as speculate on the future development of III-V compound semiconductor materials.

9:40am **SC+EL+SS-TuM5 Strain-Induced Anisotropy of Gallium Phosphide Islands on Gallium Arsenide***, **C.H. Li**,* University of California, Los Angeles*; L. Li,* University of Wisconsin, Milwaukee*; Q. Fu, M.J. Begarney, R.F. Hicks,* University of California, Los Angeles

We have undertaken a study to produce ordered nanostructures on compound semiconductor surfaces by the heteroepitaxial growth of highly strained island structures. Phosphorous-rich (2x4) islands are produced by decomposing phosphine on gallium arsenide (001)-(4x2) surfaces in ultrahigh vacuum. These islands exhibit anisotropy of approximately 10 to 1 with the (2x4) domains dramatically elongated along the [110] direction. The island width increases with the phosphorous coverage from 24 @Ao@ at 0.1 ML to 48 @Ao@) at 0.75 ML. This is attributed to strain induced by the lattice mismatch of phosphorous dimers on gallium arsenide. The implication of this finding to the epitaxial growth of GaP/GaAs heterostructure will be discussed at the meeting.

10:00am **SC+EL+SS-TuM6 Relative Reactivity of Arsenic and Gallium Dimers and Backbonds during the Adsorption of Molecular Oxygen on GaAs(100)(6x6)***, **P. Kruse**, J.G. McLean, A.C. Kummel,* University of California, San Diego

The semiconductor industry has a strong interest in understanding and employing the reactions of oxygen with III-V materials for fabrication of GaAs CMOS devices. We have monitored the initial stages of the chemisorption of molecular oxygen on the GaAs(100)(6x6) reconstructed surface by means of room temperature scanning tunneling microscopy. This surface is terminated by both gallium dimers and arsenic dimers, allowing for a direct comparison of their reactivity. Neither the As nor Ga dimer bonds react with thermal molecular oxygen. Likewise, the Ga-As back bonds of the Ga dimers do not exhibit any reactivity. Instead, the

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chemisorption proceeds with 100% chemical selectivity via the reaction of molecular oxygen with the As-Ga back bonds of the As dimers. The interaction between the highly electronegative oxygen atoms and the surface is initiated through the high electron density at the arsenic atoms. One oxygen atom displaces the attacked arsenic atom while the other oxygen atom bonds to two neighboring gallium atoms, resulting in the thermodynamically most stable reaction products: metallic arsenic clusters and gallium oxide.

10:20am **SC+EL+SS-TuM7 Role of Ligand Termination in Atomic-Layer-Controlled Growth***, **R.M. Osgood**, N. Camillone III, Y. Luo, M. Han,* Columbia University **INVITED**

We describe employment of a series of in situ UHV diagnostics to study the surface chemistry of ligand capping in limiting reactions for atomic-layer-defined growth of semiconductor thin films. In the study, molecular precursors were on surfaces held at temperatures from 180-300K in a UHV chamber. The terminating groups, formed by the dosing, were identified and their chemistry investigated using thermal desorption spectroscopy, NEXAFS, Auger, spectroscopy, and LEED. Using CdS growth on ZnSe(100) as the model system, we have found that CH@sub 3@ and H terminal groups deposited by reactions with Cd(CH@sub 3@)@sub 2@ and H@sub 2@ S, respectively, effectively limit growth precisely on all except the first monolayer. A study of intermixing in the first layer shows clearly the role of surface temperature in controlling the reaction chemistry and coverage of terminating species. The implications with regard to atomic-layer-controlled growth of other systems will also be discussed.

11:00am **SC+EL+SS-TuM9 Two-step MOCVD Growth of Piezoelectric ZnO Thin Film on SiO@sub 2@/Si Substrates***, **S. Muthukumar**, N.W. Emanetoglu, G. Patounakis, C.R. Gorla, S. Liang, Y. Lu,* Rutgers University

ZnO is a wide bandgap semiconductor with a direct bandgap of 3.3eV. Piezoelectric ZnO has high electro-mechanical coupling coefficient. Thin film piezoelectric ZnO deposited on semiconductor substrates is used for surface and bulk acoustic wave (SAW & BAW) devices, which offer advantages such as low power consumption, circuit miniaturization and cost reduction by integration with main stream MMIC technology. Furthermore, temperature compensation may be achieved in the ZnO/SiO2/Si system as ZnO and Si have positive temperature coefficient of delay (TCD), while SiO2 has negative TCD. Temperature compensated SAW devices are attractive for both communication and sensor technologies. In the present work, ZnO thin films were grown on SiO2/Si substrates by MOCVD. The structural properties of the films were investigated using XRD, SEM, and scanning probe microscopy. The films grown at 300°C were dense and had a smooth surface morphology, but poor crystallinity. In contrast, the films grown at 500°C were predominantly c-oriented, but had a rough surface. A two-step growth process was developed to obtain films with both good crystallinity and smooth surface. A high temperature (450-500°C) buffer layer was initially deposited, to provide a highly crystalline template for the subsequent low temperature (300-330°C) growth. Annealing was done on the thin films in N2 and O2 ambient for different durations to improve film resistivity, essential for fabricating low-loss SAW devices. The SAW velocity, coupling coefficient and TCD of the ZnO/SiO2/Si system were investigated through modeling and computer simulation based on Adler's transfer matrix method and Green's function analysis. The test devices with the proper ZnO and SiO2 thickness exhibited multiple temperature compensated frequency points in the 1.42 GHz to 2.15 GHz range. These results show that temperature compensated ZnO/SiO2/Si system is promising for fabricating low-loss SAW devices.

11:20am **SC+EL+SS-TuM10 Spontaneous Island Formation Caused by Reconstruction Changes During III-Sb Homoepitaxy@footnote 1@***, **A.S. Bracker**, B.Z. Nosho, B.R. Bennett, J.C. Culbertson, B.V. Shanabrook, L.J. Whitman,* Naval Research Laboratory

Most III-V semiconductor surfaces exhibit reconstructions with compositions that differ from the bulk material. These nonunity III:V stoichiometries constitute an inherent source of interfacial roughness during molecular beam epitaxy when the reconstruction changes during growth. This issue is especially important for the AlSb and GaSb(001) surfaces, because several reconstructions exist over the range of substrate temperatures and beam fluxes typically used for growth. For AlSb, the relevant reconstructions include @alpha@(4x3), @beta@(4x3), @gamma@(4x3), and c(4x4), in order of increasing Sb:Al coverage.@footnote 2@ We have used scanning tunneling microscopy (STM) and reflection high-energy electron diffraction (RHEED) to characterize how the initial stages of homoepitaxy depend on the surface reconstruction and growth conditions. When the growth conditions cause a transition between reconstructions, islands spontaneously form on the surface. In addition to roughening an otherwise flat surface, these islands change the island size distribution during subsequent growth. Unfortunately, the RHEED patterns for the three (4x3) surfaces all have a similar streaky (1x3) symmetry during growth, making it difficult to optimize growth conditions based on this diagnostic alone. However, because of its sensitivity to surface roughness, RHEED intensity oscillations may be used to monitor the reconstruction-mediated roughening. We will discuss the realistic growth situations where this type of roughening should be important. @FootnoteText@ @footnote 1@This work was supported by ONR and DARPA. @footnote 2@Barvosa-Carter et al., Phys. Rev. Lett. 84, 4649 (2000).

11:40am **SC+EL+SS-TuM11 Photon-activated Electron-Transfer-Reaction Surface Modification of GaAs(001)***, **N. Camillone III**, K.A. Khan,* Columbia University*; J.A. Yarmoff,* University of California, Riverside and Lawrence Berkeley National Laboratory*; R.M. Osgood, Jr.,* Columbia University

UHV methods for adjusting the reconstruction and composition of the top layer of atoms on a semiconductor surface are expected to have important implications for precise control of growth surfaces and surface reactions. In this talk we will describe a transformation of the surface reconstruction resulting from a photoinduced electron transfer reaction occurring thereupon. We have carried out preliminary studies which demonstrate that variation in photon exposure and thermal treatment allows the surface reconstruction to be controllably adjusted from the Ga-rich c(8x2) to the (4x6), (3x1) and As-rich c(2x8) terminations. The modification of the reconstruction is the result of a modification of the surface stoichiometry due to the extraction of surface Ga atoms as a result of reaction with bromine. The bromine is produced at the surface by photoinitiated dissociative electron attachment to methyl bromide molecules physisorbed in a single monolayer at ~ 90 K. Subsequent to the photoinduced surface reaction, the gallium is removed by annealing to desorb a gallium bromide product. A comparison of the results obtained with low energy electron diffraction, temperature programmed desorption and energy-resolved photofragment angular distribution measurements shows that the most As-rich surface obtained by our technique is identical in structure to that of a control surface prepared using the standard iodine thermal reaction method. In principle, the use of this photon-activated reaction, and others like it, could allow for precise patterning of the surface structure based on control of photon or electron exposure, molecular coverage, thermal treatment and lateral patterning of the incident photon or electron beam.

Surface Engineering
Room 201 - Session SE-TuM

Interface Engineering and Graded Films: Structure and Characterization

Moderator: I. Petrov, University of Illinois, Urbana

8:40am **SE-TuM2 Epitaxial Growth of Metastable B1-NaCl-Structure TaN@sub x@ on MgO(001) by Ultrahigh Vacuum Reactive Magnetron Sputter Deposition***, **C.-S. Shin**, D. Gall, J.E. Greene, I. Petrov,* University of Illinois

Metastable B1-NaCl-structure TaN@sub x@ (x = 1-1.3) layers, with thicknesses 0.25 to 0.5 @micro@m, were epitaxially grown on MgO(001) at temperatures T@sub s@ between 600 and 700 °C by ultra-high-vacuum reactive magnetron sputtering in N@sub 2@/Ar mixtures. X-ray diffraction and transmission electron microscopy results show that the epitaxial relationship is cube-on-cube, (001)@sub TaN@||(001)@sub MgO@ with [100]@sub TaN@||[100]@sub MgO@. TaN@sub x@ layers grown at T@sub s@@>=@ 700 °C undergo a transition from the metastable NaCl structure to the thermodynamically-stable hexagonal phase. NaCl-structure TaN@sub x@ layers with x = 1-1.22 exhibit a nearly constant resistivity of 225 @micro@@OHM@-cm with hardness (H) and elastic modulus (G) values, determined by nanoindentation, of 31±0.9 and 457±16 GPa, respectively. Higher N/Ta ratios lead to an increase in @rho@ and a decrease in H and G. All cubic TaN@sub x@ layers exhibit negative temperature coefficients of resistivity between 20 and 400 K due to weak carrier localization. TaN@sub x@ is superconducting with the highest critical temperature, 8.45 K, obtained when x is close to 1.

9:00am **SE-TuM3 Stress Evolution in TiN and TaN Layers and Multilayers Prepared by Reactive Magnetron Sputtering and Studied with in-situ Laser Reflection Curvature Technique*, T. Joelsson,*** *J. Birch, P. Sandström, L. Hultman,* IFM Linköping University, Sweden

TiN and TaN are interesting materials for an industrial purpose both as hard coatings and as contact materials and diffusion barriers in microelectronics. Control and understanding of the stress evolution in these films is of importance since problems such as delamination and cracking may occur due to compressive and tensile stresses. We have used time-resolved in-situ curvature technique to measure the stress evolution during UHV magnetron reactive sputter deposition onto Si wafers. 800 nm thick individual layers of TaN and TiN have been studied at different nitrogen partial pressures during growth. For TaN at low nitrogen partial pressures, the stress evolution is first tensile with a maximum level of around 0.5 GPa then after 30 nm it turns compressive. At higher nitrogen partial pressures the TaN layers are always compressive. For TiN the layers starts to grow compressive and then turns tensile. For TiN in multilayer and at low nitrogen partial pressure (0.45 mTorr) first a tensile stress is developed then a compressive and finally a tensile stress. This can be correlated with the coalescence stages. The initial compressive state seen in the TiN films is probably correlated to heating of the sample due to bombardment of energetic species (approximately 40° C). When TiN and TaN are deposited sequently to form a multilayered structure the overall residual stress is determined by the thickness of the individual layers and the eventual thermal relaxation time between the different layers. TaN also exhibits phase transformations as a function of layer thickness in a multilayer stack, which in turn offsets the stress evolution.

9:20am **SE-TuM4 The Compressive Coating Stresses in the Scratch Adhesion Test*, Y. Xie,*** *H.M. Hawthorne,* National Research Council Canada, Canada

Despite the widespread use of the scratch adhesion test, there is no model available to determine the critical coating stress for initiating interfacial failure, so that ranking the coating-substrate adhesion of coated systems with different mechanical properties is impossible. In this study, a mathematical model is developed to calculate the distribution of compressive stresses in a thin coating induced by a scratch indenter. For ease of use in practice, a simple equation, @sigma@@sub cm@ = 0.15 (P@sub c@H@sub f@/H)@super 0.5@ E@sub f@@super 0.3@ E@super 0.2@/R, is then derived from the model, where @sigma@@sub cm@ is the critical mean compressive stress in the coating for interfacial failure, P@sub c@ is the critical normal load measured from the scratch adhesion test, H@sub f@ and E@sub f@are the hardness and Young's modulus of the coating, H and E are the hardness and Young's modulus of the substrate, and R is the indenter radius. This equation is useful for ranking the coating-substrate adhesion of different coated systems, or, for estimating the critical mean coating stress for interfacial failure.

9:40am **SE-TuM5 Interface Engineering and Graded Films: Structure and Characterisation*, S.J. Bull,*** University of Newcastle, U.K. **INVITED**

The properties and performance of most bulk materials and coatings are controlled by interfaces. For bulk materials the surface is the most important interface, though grain and phase boundaries may also play a role in dictating performance. However, when developing coating systems there is the possibility of using many interfaces to control behaviour. As well as the surface, the coating/substrate interface will be important and in multilayer coating designs the number and properties of the individual layer interfaces will also play a role. It has often been observed that multilayer coatings offer enhanced hardness and fracture resistance compared to comparable single layer coatings though the reasons for these improvements are not always well understood. This paper will review the effect of interfaces on the mechanical properties and tribological performance of bulk materials, single and multilayer coatings highlighting the importance of engineering interfaces with high strength if coatings with optimum properties are to be achieved. A simple model will be introduced which enables the effect of such interfaces to be more fully appreciated. The possibility of using graded compositions to improve performance will be discussed in light of this model.

10:20am **SE-TuM7 Characterization of Cr@sub 2@N/CrN Multilayer Coatings Produced by Ion-Assisted Reactive Magnetron Sputtering*, S.M. Aouadi,*** University of Nebraska*; K.C. Wong, K.A.R. Mitchell,* University of British Columbia, Canada*; S.L. Rohde,* University of Nebraska

A series of monolithic and multilayer coatings of chromium nitride with various compositions and architectures were deposited at low temperatures (<200°C) on silicon substrates using ion-assisted reactive magnetron sputtering. Real-time in-situ ellipsometry was used to control the deposition process. The multilayer coatings were fabricated with a CrN to Cr@sub 2@N ratio in the range from 1 to 12. In addition, the deposition parameters were altered to obtain interfacial geometries that varied from sharp to various levels of grading. The deposited coatings were characterized post-deposition using X-ray diffraction (XRD), Rutherford backscattering (RBS), X-ray photoelectron spectroscopy (XPS), and ex-situ spectroscopic ellipsometry (SE). The crystal phases and textures were identified using XRD. The film composition, the periodic structure of the multilayers and the interface type were determined from RBS, XPS and SE measurements. To compare the mechanical properties of the coatings, their hardness was evaluated using a nanoindenter. Most coatings gave hardness values in excess of 20 GPa.

10:40am **SE-TuM8 Optimization of In Situ Substrate Surface Treatment in a Cathodic Arc Plasma: A Plasma Diagnostics and STEM-EDX Study*, C. Schönjahn,*** *A.P. Ehiasarian, W.-D. Münz, D.B. Lewis, R. New,* Sheffield Hallam University, UK*; R.D. Twesten, I. Petrov,* University of Illinois, Urbana

It has been shown previously that the in situ substrate cleaning step prior to PVD deposition affects the interface formation which influences the adhesion of the coating on the substrate. Most promising results were obtained for Cr ion bombardment where the Cr ions are extracted from a cathodic arc source by negatively biasing the substrates with U@sub s@=-1200V. The main objective of the current project is a further optimization of the in situ substrate surface pre-treatment with respect to reduced process costs and lower risk for local substrate overheating. Langmuir probe measurements show that the presence of Ar leads to a two-fold increase of the speed of the cathode spot thus reducing the amount of macro particles emitted by the cathodic arc source. The presence of Ar leads to an increased ion current density of j = ~30 Am@super -2@ for P@sub Ar@ = 8x10@super -2@ Pa compared to j = 6 Am@super -2@ at background pressure of P@sub tot@ = 7x10@super -4@ Pa due to the ionization of Ar in the cathode spot and in charge exchange reactions with Cr ions as observed by Optical Emission Spectroscopy. Although the mean energy of bombarding species decreases the higher ion flux suggests a more effective removal of substrate material. This is indeed observed by measuring an effective etching rate of 4 nm.min@super -1@ at P@sub tot@ = 7x10@super -4@Pa compared to 8 nm.min@super -1@ at P@sub Ar@ = 8x10@super -2@Pa. However, owing to the loss of high energy Cr ions, metal ion implantation, which was shown to be beneficial for adhesion, is reduced. The implantation profiles were studied by STEM-EDX analysis on electron transparent cross sections. Based on these results a two stage ion bombardment procedure is proposed. The first stage is Cr bombardment at an Ar pressure of 8x10@super -2@ Pa for intensive cleaning. This is followed by pure Cr ion bombardment for enhanced ion implantation due to the higher portion of multiply charged Cr ions to achieve enhanced adhesion.

11:00am **SE-TuM9 Laterally Graded Multilayers and their Applications@footnote 1@*, C. Liu,*** *A. Macrander,* Argonne National Laboratory*; J. Als-Nielsen,* Copenhagen University, Denmark*; K. Zhang,* Illinois Institute of Technology

Laterally graded multilayers consisting of uniform W layers and wedge-shaped C layers have been made at the Advanced Photon Source (APS) deposition lab for tunable x-ray double-monochromator applications. The double monochromator has two identical graded multilayers in series, as in the conventional double-crystal monochromator arrangement. By letting the x-ray beam hit slightly different (bilayer) d spacing on each multilayer, one can adjust the bandpass and peak energy of the transmitted beam. Also, since that the Bragg angles of the two multilayers are not constrained to be the same, the angle of the transmitted beam can be varied in the vertical plane. This option may be an attractive alternative to the conventional way for studying liquid surfaces in reflectivity and grazing incidence diffraction measurements. The graded multilayer comprised 60 bilayers of W and C on 100 x 25 x 3 mm float glass with a d spacing varying from 35 to 60 Å and an average gradient of 0.27 Å/mm along the long direction. The films were made by DC magnetron sputtering with the sputtered atoms passing a contoured mask while the substrate was moving. Two different masks were designed to produce either a uniform (for W) or graded (for C) thickness profile. The multilayer and graded multilayers have many other novel applications. Potential applications in x-ray fluorescence detection and x-ray standing wave experiments will be discussed. @FootnoteText@@Footnote 1@This work is supported by the U.S. Department of Energy, BES, under contract no. W-31-109-ENG-38

11:20am **SE-TuM10 A Novel Interface Modification Technique Applied from the Top of a Coated Layer**, ***M. Yoshitake***, *Y.-R. Aparna, K. Yoshihara,* National Research Institute for Metals, Japan

A technique to modify interface after the formation of interface is desired either from a process requirement or because of the change of material use with time. A novel technique to form an intermetallic compound at the interface between coated layer and substrate by depositing a chosen metal film on the top of a coated layer is presented. Based on the property of the intermetallic compound, an interface is modified. Experimentally, the diffusion and interfacial reaction of specimens with top-film/middle-film/substrate structure were investigated. With proper choice of top-film element, top-film element diffuses inside without detectable reaction with middle-film and concentrate at the interface between middle-film and substrate followed by intermetallic compound formation. We discuss conditions for obtaining above phenomena and general guide for a choice of top-film element is presented. Key factors are (1)segregation tendency of top-film element on middle-film metal, (2)activation energy of diffusion of top-film element in middle-film and in substrate and (3)formation of intermetallic compound between top-film metal and substrate in phase diagram. The examples of intermetallic compound formation by the diffusion of top-film element are given in Ti-film/Nb-film/Cu-substrate, Fe-film/Nb-film/Ti-substrate and other combinations.

Surface Science
Room 208 - Session SS1-TuM
Reactions on Oxides and Environmental Chemistry

Moderator: C.H.F. Peden, Pacific Northwest National Laboratory

8:20am **SS1-TuM1 Ethylene Polymerization on a CrOx/SiO2 Model Catalyst: XPS, SIMS, RBS and AFM**, ***P.C. Thuene***, *J. Loos,* Eindhoven University of Technology, The Netherlands; *J.W. Niemantsverdriet,* Eindhoven University of Technology, The Netherlands, Netherlands

Achieving realistic catalytic activity on a model catalyst consisting of Cr on 1 cm2 of planar SiO2 at a loading of 1 Cr per nm2 has proven to be the major challenge in designing a surface science model for the Phillips ethylene polymerization catalyst. Poisons like water or acetylene can deactivate the catalyst within a fraction of a second even if they are present in minute (1ppm) quantities. By using special filters we can now run polymerization reactions at 160Â°C for at least 30 minutes without deactivation of the catalyst. The polymer yield after each polymerization run is measured most conveniently by analyzing scalpel scratches with atomic force microscopy (AFM). The catalyst shows a constant activity with a pseudo turnover frequency of 2.5 C2H4 / Cr s. This corresponds to 250 g PE / gcat h atm if rescaled to the surface area of an industrial catalyst (286 m2/g, Crossfield) which represents a realistic catalytic activity. Owing to the planar geometry, the state of Cr can be determined in detail by using XPS and SIMS, while the polymer morphology can be analyzed with AFM.

8:40am **SS1-TuM2 Structurally Ordered Magnesium Vanadate Model Catalysts for Oxidative Dehydrogenation**, ***A.G. Sault***, *J.E. Mudd, J.A. Ruffner, J.E. Miller,* Sandia National Laboratories

A fundamental understanding of active sites in mixed metal oxide oxidative dehydrogenation (ODH) catalysts continues to be elusive. In an effort to simplify the complexities inherent in these materials we are growing single phase, oriented mixed metal oxide thin films. Using RF sputter deposition, we have grown 10-2000 Å films of Mg@sub 3@(VO@sub 4@)@sub 2@, a known ODH catalyst. Bulk and surface analysis of films grown on silicon wafers show the desired stoichiometry, but the films are amorphous. Deposition on a 500 Å gold layer grown on oxidized silicon results in films strongly oriented toward the (021) plane of Mg@sub 3@(VO@sub 4@)@sub 2@. This orientation is due to the tendency of gold to grow with (111) planes exposed, which provides an ideal epitaxial substrate for Mg@sub 3@(VO@sub 4@)@sub 2@ (021). This plane consists of close packed oxygen layers, with Mg and V ions in octahedral and tetrahedral sites, respectively. By varying oxygen pressure we can deposit films with stoichiometries ranging from fully oxidized Mg@sub 3@(VO@sub 4@)@sub 2@ to partially reduced Mg@sub 3@V@sub 2@O@sub 6@. We will detail the effects of heat treatments in reactive environments (e.g., oxygen/propane mixtures) on the structure and composition of these films, and report on the catalytic activity of these films for ODH. In general, heating the films above 623 K in vacuum or 100 Torr propane results in at least partial reduction of V(V) to V(III) and segregation of V to the surface. Prolonged reduction at higher temperatures results in complete reduction to Mg@sub 3@V@sub 2@O@sub 6@. Treatment in oxygen reverses these changes. This reversible redox chemistry is consistent with the known mechanism for ODH, which involves participation of lattice oxygen. Catalytic measurements of propane ODH show very low conversions due to the low surface areas of the films. Measurements with more facile ODH reactions (such a 1-butene to butadiene) are underway and will be reported.

9:00am **SS1-TuM3 Reactive Scattering Studies of Organophosphorous Compounds on Semiconducting Metal Oxides**, *J.L. Duncan, S. Ma, R.H. Jackson,* ***B.G. Frederick***, University of Maine

Semiconducting metal oxides (SMOs) are promising materials for the development of conductivity-based chemical sensors with a broad range of applications. The reactions of organophosphorous compounds are of interest for detection of pesticides and nerve agents. Improvement of the selectivity of SMO sensors requires an understanding of the steps in the decomposition or reaction mechanism which lead to changes in conductivity. We present results of reactive, molecular beam scattering studies for dimethyl methyl phosphonate (DMMP), and related compounds from tungsten oxide based sensors. The experiments utilize molecular beam doser sources with known flux distributions and a differentially-pumped, calibrated mass spectrometer system allowing the coverage, sticking coefficients, and reactive scattering probabilities to be quantified. Reactive scattering of methanol, formic acid, trimethyl phosphine oxide, and trimethyl phosphonate, contribute to understanding the decomposition mechanism of DMMP and the associated conductivity changes observed in the SMO films.

9:20am **SS1-TuM4 Chemistry of SO@sub 2@ and NO@sub 2@ on ZnO(0001)-Zn and ZnO Powders: Changes in Reactivity with Surface Structure and Composition**, ***J.A. Rodriguez***, *T. Jirsak, J. Dvorak, J. Hrbek,* Brookhaven National Laboratory

Synchrotron-based photoemission and x-ray absorption spectroscopy have been used to study the interaction of SO@sub 2@ and NO@sub 2@ with ZnO(0001)-Zn and polycrystalline surfaces of zinc oxide (films and powders). Important differences are observed when comparing the behavior of the adsorbates on these oxide surfaces. These differences are in a part a result of changes in structural properties (flat vs rough surfaces), but in some cases they clearly originate in variations in surface composition (Zn-adsorbate vs O-adsorbate interactions). For example, the Zn-terminated (0001) face of ZnO interacts weakly with SO@sub 2@ (desorption temperature of adsorbate < 200 K). In contrast, the SO@sub 2@ molecules interact readily with O sites of Ar@super +@ sputtered ZnO(0001)-Zn or polycrystalline ZnO forming very stable SO@sub 3@ species. Due to its radical nature, adsorbed NO@sub 2@ is more chemically active than SO@sub 2@. After dosing nitrogen dioxide to ZnO(0001) at 100 K, chemisorbed NO@sub 2@ and NO@sub 3@ coexists on the surface. Partial transformation of NO@sub 2@ into NO@sub 3@ is observed from 150 to 300 K. The data for the NO@sub 2@/ZnO(0001)-Zn system clearly prove that large quantities of NO@sub 3@ can be formed on metal sites of an oxide surface as a consequence of partial decomposition or disproportionation of NO@sub 2@.

9:40am **SS1-TuM5 Adsorption of S and Cl on TiO@sub 2@(110) Studied by Ultra-violet Photoelectron Spectroscopy**, *E.L.D. Hebenstreit, W. Hebenstreit, U. Diebold,* Tulane University; *H. Geisler,* Xavier University; *D.A. Hite, P.T. Sprunger,* Louisiana State University; *S.N. Thornburg,* ***C.A. Ventrice, Jr.***, University of New Orleans

One of the most severe poisonings of metal and metal oxide catalytic systems is induced by sulfur contamination. In order to obtain a better knowledge of the mechanism for contamination of catalysts at a microscopic level, an ultra-violet photoelectron spectroscopy (UPS) study of the adsorption of elemental S and Cl on reduced TiO@sub 2@(110) surfaces has been performed. A previous study of the adsorption of S on TiO@sub 2@(110) has shown that a variety of overlayer structures can be obtained, depending on the temperature of adsorption.@footnote 1@ Below ~120 °C, S adsorbs preferentially on the exposed Ti rows and forms a weakly ordered overlayer. Above ~120 °C, there is a change in the S adsorption site from on top of the Ti rows to a replacement of the surface O. UPS measurements show that the surface defect state of the reduced TiO@sub 2@ substrate is quenched upon adsorption of S at RT. In addition, there is a shift of 0.4 eV in the valence emission to lower binding energy that results from an "un-bending" of the valence band. Adsorption of S at ~350 °C results in an enhancement of the surface defect state and the appearance of new emission features within the band gap of the TiO@sub 2@. Both the defect state and the emission features within the band gap resonate at the Ti 3p to 3d absorption threshold. A shift in the Ti 3p core emission of ~0.5 eV to lower binding energy and a reduction in the O 2s emission are also observed. These results indicate that there is an increase in the population of Ti 3d states from a loss of surface O. Cl adsorption at RT behaves similarly to S with a quenching of the surface defect state and a 0.4 eV shift of the valence band. Although adsorption of Cl at 200 °C results in an enhancement of the surface defect state, no new emission features are observed within the band gap of the TiO_2. [1] E. L. D. Hebenstreit, W. Hebenstreit, and U. Diebold, Surf. Sci. (in press).

10:00am **SS1-TuM6 Thermal Production of Phosgene from Carbon Tetrachloride Reactions on Natural Single Crystal α-Fe_2O_3 Surfaces in Ultrahigh Vacuum**, ***K. Adib***, *N. Camillone III, J.P. Fitts, D. Mocuta, K.T. Rim, G.W. Flynn, R.M. Osgood, Jr.,* Columbia University; *S.A. Joyce,* Pacific Northwest National Laboratory

Oxides of iron have important applications as catalysts and reactive sites for various classes of chemical reactions. They have a significant environmental role in the speciation of toxic metal cations and the dehalogenation of halocarbons. This environmental role is important due to the abundance of iron oxides in the Earth's crust and due to their higher reactivity compared to other metal oxides. We use ultrahigh vacuum for a detailed study of the chemistry of a well-characterized surface of α-Fe_2O_3 (hematite). Natural single crystal samples of hematite were cut and polished in the (0001) orientation. They were processed in-situ to produce a surface selvedge of Fe_3O_4 2x2 reconstruction, as verified by LEED, and dosed at ~100K with CCl_4. The surface reactions were studied by temperature-programmed desorption (TPD). The multiplicity of desorption waves observed indicates a complex chemistry involving molecular adsorption and dissociative adsorption on at least two distinct kinds of surface site. The TPD results indicate the formation of $COCl_2$ (phosgene) as well as C_2Cl_4 and high temperature desorption of iron chlorides. We observe significant differences in the TPD spectrum following the first dosing of the surface as compared to those measured following subsequent dosings indicating a marked change in the surface upon initial exposure. This change is commensurate with the titration of surface defects during the initial reaction stages. Preliminary measurements of the UV photochemistry of the adsorbed CCl_4 on this surface will be presented.

10:20am **SS1-TuM7 Multiplet Splitting and Crystal Field Strengths at Iron Oxide Surfaces**, ***T. Droubay***, *S.A. Chambers,* Pacific Northwest National Laboratory; *B.P. Tonner,* University of Central Florida

The metal core-level spectra of 3d-transition metal oxides exhibit complex lineshapes due to multiplet splitting in the final state. The crystal field splitting largely determines the degree of multiplet structure. We have measured surface and bulk-sensitive Fe 2p core-level spectra at high energy resolution for several MBE-grown iron oxide epitaxial films. Line shape differences are observed between surface and bulk sensitive photoemission spectra, indirectly revealing differences in crystal field strength. In order to determine the surface crystal field strength, we have utilized XAS L-edge spectra of bulk iron oxides, and have calculated these spectra from first principles using an atomic multiplet theory. Agreement of ultra-high resolution experimental absorption spectra and theoretical models is excellent. We then used the theoretical multiplet model to simulate the bulk-sensitive XPS core-level spectra by broadening to account for the increased lifetime and adjusting peak heights to optimize agreement between theory and experiment. This step produced an accurate value for the bulk crystal field strength. The metal ion site symmetry was then reduced in the calculation and agreement re-optimized between theory and surface sensitive XPS spectra to obtain the equivalent surface crystal field strength. Determination of the crystal field strength at the surface may provide an insight into oxide surface reactivity.

10:40am **SS1-TuM8 Scanning Electron Microscopy Studies of the Hydration of Alkali Halides**, ***S.A. Joyce***, *J.P. Cowin,* Pacific Northwest National Laboratory

Morphological and phase changes of several salts which are important constituents of sea-salt aerosols were examined in an environmental scanning electron microcospe as function of both water vapor pressure (from ~2 to 18 Torr) and temperature. For highly soluble materials, dissolution can occur by incorporation of water from the gas phase. The dissolution of NaCl and NaBr samples upon exposure to water vapor have been imaged and the observed temperature dependence of the deliquescence pressures agree well with previous studies. The deliquescence is initially observed as the surface of a crystal becomes featureless, followed by a rounding and spreading of the solution droplet on the sample holder. NaBr converts to the dihydrate ($NaBr*2H_2O$) at water pressures roughly half the deliquescence pressure. The formation of the hydrate can be readily observed in the SEM. Unlike the case of deliquescence, no significant changes in the microtopography are initially observed, rather hydration results in a change in the contrast. Dark regions on the surface nucleate and grow as the hydration proceeds. The rate of hydration/dehydration is a strong function of the pressure (i.e. the saturation ratio). Prolonged hydration results in an increase in the roughness of the surface presumably due to microcrystallite formation as a stress-relief mechanism. Cycling hydration/dehydration results in higher roughness. Delamination and spalling have been observed upon rapid dehydration. Both effects increase the net surface area. Such cycling is very common in the atmosphere versus changes in altitude, time, and the day/night cycle, and should have a strong impact on water-soluble aerosol morphology. * Pacific Northwest National Laboratory is operated for the Department of Energy by Battelle under Contract DE-AC06-76RLO 1830.

11:00am **SS1-TuM9 Reactivity of Water toward NaCl(100)**, ***A.J. Leavitt***, *R.D. Huffstetler, Jr., J.W. Russell, J.I. Brauer, J.K. Cutchins, C.D. Lane, M.B. Reddy, F.A. Khan,* State University of West Georgia

The role of water-mediated reactions that occur on particulate NaCl surfaces is relevant to atmospheric chemistry. A temperature-programmed desorption (TPD) study of water adsorbed onto NaCl(100) was performed. Water was adsorbed onto the surface held at a temperature of 130 K at a variety of water fluences, then thermally desorbed into a quadrupole mass spectrometer in an ultrahigh vacuum chamber. Water molecularly adsorbs onto the surface and desorbs in a first-order process at ~143 K for fluences corresponding to 10% of a monolayer. As the water fluence is increased, the temperatures of maximum desorption shifts higher suggesting stabilization of the water layer through hydrogen bonding. Further increases in water fluences lead to a constant area under the desorbing peak suggesting the buildup of a condensed layer of the water on the NaCl surface. This desorption feature does not appear to saturate at very high fluences of water. These results are consistent with previous work by Falsch and Henzler (UPS study) and Peters and Ewing (IR study). This work was supported by Research Corporation.

11:20am **SS1-TuM10 Surface Segregation of Bromine in Bromide Doped NaCl: Implications for the Seasonal Variations in Arctic Ozone**, ***S. Ghosal***, *J.C. Hemminger,* University of California, Irvine

Episodes of ozone depletion attributed to chemistry of gas phase bromine compounds in marine regions of the Arctic boundary layer have been reported at polar sunrise. Models for the source of brominated compounds in the marine Arctic troposphere have focussed on surface chemistry of sea salt ice and aerosols even though the molar ratio of Cl^- to Br^- in sea salt is expected to be ~660 to 1. X-ray photoelectron spectroscopy (XPS) studies described here show, for the first time, substantial segregation of Br^- to the surface of NaCl samples with low level Br^- dopant. Water exposure plays an important role as it provides enhanced ionic mobility in such systems allowing the surface segregation as the system approaches thermodynamic equilibrium. Our XPS results are confirmed by scanning electron microscopy (SEM) imaging of the salt sample surface after water vapor exposure, which shows NaBr crystallites that form at the surface. Our experiments provide the first experimental evidence of surface segregation in mixed alkali halide solids.[1] The segregation phenomenon displayed here is likely to play an important role in a wide range of atmospheric phenomena that involve surface reactions of sea salt particles and aerosols. [1] This work was supported by the NSF Grant ATM-9707285.

11:40am **SS1-TuM11 Isothermal Desorption Kinetics of H_2O from $^{1}H_2{}^{16}O$, $^{1}H_2{}^{18}O$ and $^{2}H_2{}^{16}O$ Ice Multilayers**, ***J.A. Smith***, *F.E. Livingston, S.M. George,* University of Colorado at Boulder

The mechanism of H_2O desorption from ice can be explored by examining the H_2O desorption kinetics from ice composed of the various H_2O isotopomers. The isothermal desorption kinetics of H_2O from $^{1}H_2{}^{16}O$, $^{1}H_2{}^{18}O$ and $^{2}H_2{}^{16}O$ ice multilayers were measured using optical interferometry. These experiments were performed at temperatures between 175-195 K using ice multilayers grown epitaxially on a Ru(001) surface. The desorption rates of $^{1}H_2{}^{16}O$ and $^{1}H_2{}^{18}O$ were very similar. The desorption kinetics for ^{1}H

2@@super 16@O were E@sub d@ = 13.9 +/- 0.2 kcal/mol and @nu@@sub d@ = 10@super 32.6 +/- 0.3@ molecules/cm@super 2@ s. In contrast to the expectation that the H@sub 2@O desorption rate should scale with the square root of molecular mass, the desorption rate of @super 2@H@sub 2@@super 16@O was approximately a factor of two slower over the measured temperature range. The desorption kinetics for @super 2@H@sub 2@@super 16@O were E@sub d@ = 14.8 +/- 0.4 and @nu@@sub d@ = 10@super 33.4 +/- 0.5@ molecules/cm@super 2@ s. The desorption kinetics for the three H@sub 2@O isotopomers are explained using transition state theory. Th e rotational degrees of freedom yield the main differences. The differences in the activation energies are related to the zero-point energies of frustrated rotations on the ice surface. The differences in pre-exponentials are associated with the moments of inertia of the desorbing molecules.

Surface Science
Room 209 - Session SS2+NS+BI+EL-TuM
Self-Assembled Monolayers

Moderator: D.H. Fairbrother, Johns Hopkins University

8:20am **SS2+NS+BI+EL-TuM1 Creating Highly Selective Organic Surfaces using Self-assembly: A New Family of Organothiols*, R. Arnold,*** Ruhr-Universität Bochum, Germany*; A. Terfort,* Universität Hamburg, Germany*; C. Wöll,* Ruhr-Universität Bochum, Germany

The creation of organic surfaces with specific properties via the adsorption of correspondingly functionalized organothiols has recently attracted considerable interest, e.g. in the context of bio-sensors and biomimetics. In case of alkanethiols some functional groups, however, interact so strongly with each other that the ordering within the SAMs is affected, e.g. in the case of -COOH functional groups.@footnote 1@ The situation can be improved by using more rigid backbones, e.g. oligophenyl units.@footnote 2@ With regard to biochemical applications in many cases the distance between adjacent organothiol units (4.97 Å) is too small to immobilize larger molecules, e.g. small proteins. In the past these problems could be overcome in some cases by diluting the functionalized organothiol in a shorter, nonfunctionalized thiol. Here, we present a different approach where a more bulky thiol is used, which increases the nearest neighbor distance. We will present the results of a study using several homologues of triptycenethiols. SAMs formed from these compounds were characterized by using XPS, IRRAS, NEXAFS, LEED and TDS. The results reveal the formation of well ordered monolayers, which are anchored to the gold surface in a more distant lateral structure than alkane- or p-terphenylthiols. @FootnoteText@ @footnote 1@ Dannenberger, O.; Weiss, K.; Himmel, H.-J.; Jäger, B.; Buck, M.; Wöll, C. Thin Solid Films 1997, 307, 9885-9893 @footnote 2@ Himmel, H.-J.; Terfort, A.; Wöll, C. J. Am. Chem. Soc. 1998, 120, 12069-12074.

8:40am **SS2+NS+BI+EL-TuM2 Characterization of the Alkanthiol/Metal Interface by High Resolution Core Level Spectroscopy*, K. Heister,*** *H. Rong, M. Buck,* University Heidelberg, Germany*; L. Johansson,* University Karlstad, Sweden*; M. Zharnikov, M. Grunze,* University Heidelberg, Germany

During the last decade X-ray Photoelectron Spectroscopy with a laboratory X-ray source became a conventional technique to characterize thiol derived SAMs. However, due to the mostly poor energy resolution, a strong attenuation of the photoelectron signal, and a low photoionization cross-section of the relevant core levels at high photon energies a precise binding energy analysis of an important building block of a SAM, the SAM/metal interface was hardly possible, even though high resolution photoelectron spectroscopy could give important information about the chemical state of the atoms in this region. Taking advantage of the high performance and tunebility of the third generation synchrotron sources we have firstly applied the synchrotron-based High Resolution Core Level Spectroscopy to study the SAM/metal interface. The variable photon energy of the synchrotron light and a high energy resolution of the spectrometer (0.1-0.3 eV) enabled us to resolve the bulk and surface components of the substrate emission peak (Au 4f / Ag 3d) and monitor the evolution of these components upon the alkanethiol and biphenylthiol adsorption. Simultaneously, the interaction of the thiol-derived molecules with the substrate was followed by monitoring the S2p doublet attributed to the sulfur head group of these molecules. Only one sulfur species was found in the densely packed SAMs, which implies an equivalent bonding geometry for all adsorbed molecules. In SAMs comprising of specially designed, mixed aliphatic-aromatic molecules a periodical, 'odd-even' shift of the S2p binding energy with the varying length of the aliphatic part was observed. This shift can be attributed to the distortion of the substrate-S bonding angle resulting from the unfavorable package conditions occurring at definite lengths of the aliphatic part. This work has been supported by the German Bundesministerium für Bildung, Wissenschaft und Technologie through grant No. 05 SL8VHA 2 and by DAAD.

9:00am **SS2+NS+BI+EL-TuM3 The Influence of the Endgroup and the Chain Length on the Growth of CH@sub 3@- and CF@sub 3@-terminated Alkanetiols on Au(111)*, J. Pflaum,*** Princeton University*; G. Bracco,* University of Genova, Italy*; G. Scoles,* Princeton University*; R. Lee,* University of Houston*; A. Kahn,* Princeton University

The influence of the functional endgroup and the CH@sub 2@ chain length on the growth of alkanethiols on Au(111) was studied by scanning tunneling microscopy (STM) and x-ray surface diffraction in grazing-incidence geometry (GIXD). Thiols are model systems for self-assembled monolayers (SAMs) and exhibit a complex phase diagram as function of coverage. The structure and the electronic properties of the SAMs are determined by the sulfur headgroup, the CH@sub 2@ backbone and the functional endgroup. Leaving the sulfur headgroup unchanged, we studied how the film structure depends on the endgroup by comparing CH@sub 3@- and CF@sub 3@-terminated thiols. All films were prepared from solution on an atomically ordered Au(111) surface. The lateral order of the as-grown CH@sub 3@-terminated films corresponds to the c(4x2) phase, i.e. the highest density standing-up phase. From STM studies we conclude that the arrangement of CH@sub 3@ endgroups corresponds to a pinwheel-like structure rather than to a zig-zag-like structure. In contrast, CF@sub 3@(CH@sub 2@)@sub 9@SH showed no lateral ordering as seen by STM and GIXD. However, the difference between electron densities at the CF@sub 3@/vacuum and the SH/Au interfaces induces an oscillation of the GIXD reflectivity. Fitting the periodicity of the modulation using the Parratt formalism leads to an estimate of the film thickness and its roughnesses at both interfaces. In spite of the lack of lateral order the film appears to be made by standing-up molecules. Differences between the thickness measured by ellipsometry and x-rays will be discussed. We will also explore the lying-down phase of alkanethiols and fluorinated thiols as organic templates for organic heterostructures. Initial results on the growth of PTCDA on such templates will be presented. This work was supported by the MRSEC program of the National Science Foundation (DMR-9809483). J.P. thanks the Deutsche Forschungsgemeinschaft for support (Grant No. PF 385/1-1).

9:20am **SS2+NS+BI+EL-TuM4 Self-Assembled Monolayers of Terphenyl Derivatized Thiols; Adsorption, Insertion Process and Electrical Conduction*, T. Ishida,*** JRCAT-NAIR and PRESTO-JST, Japan*; W. Mizutani,* JRCAT-NAIR, Japan*; N. Choi,* JRCAT-ATP, Japan*; H. Tokumoto,* JRCAT-NAIR, Japan

The investigation of SAMs made from conjugated molecules is highly activated from a viewpoint of molecular electronics as well as stable SAM formation. In the present study, we have investigated an insertion process of conjugated molecules, terphenylthiol (TP0), terphenyl methanethiol (TP1), terphenyl propanethiol (TP3), into nonanethiol self-assembled monolayers (SAMs) on Au(111) by STM. STM observation revealed that the insertion process is dependent on the molecular length of conjugated molecules. At the initial stage of insertion, replaced area of TP1 is larger than those of TP0 and TP3. However, when the immersing time is more than 12h, the replaced area of TP3 is larger than those of TP0 and TP1. The insertion process is likely to be determined by the solubility of the conjugated molecules and thermal dynamics. The single molecular resistance were increased with the number of the methylene groups, and obtained about 20G-ohm (TP0), 40 G-ohm (TP1) and 66 G-ohm (TP3). The vertical conduction of the conjugated molecular domains of TP1 and TP3 depended on their lateral sizes, while strong dependence was not observed in the case of TP0, suggesting that methylene group is necessary between the sulfur and aromatic rings to increase the vertical conduction of molecular domain.

9:40am **SS2+NS+BI+EL-TuM5 Structure and Chemistry of Alkanethiol Self-Assembled Monolayers*, G.E. Poirier,*** *T.M. Herne, C.C. Miller, M.J. Tarlov,* National Institute of Standards and Technology **INVITED**

Derivatized alkanethiols form dense, physically blocking films on Au surfaces thereby providing an effective and parsimonious method to control the chemical, physical, and electron-transfer properties of electrode surfaces. To predict the function of these monolayers in device applications, scientist require an understanding the molecular-scale structure and chemistry. Our structure studies were conducted using gas-phase transport of decanethiol onto clean Au(111). Characterization was accomplished using ultrahigh vacuum scanning tunneling microscopy. At low surface coverage, decanethiol exists as a 2-dimensional gas. With increasing coverage the molecules sequentially condense into islands of three discrete commensurate crystalline lattices, each characterized by alignment of the molecular axes with the surface plane (striped phases). Above saturation coverage of the densest striped phase, the monolayer undergoes an edge-mediated melting transition forming a supercooled 2-dimensional liquid. Domains of the c(3x2*3) phase, characterized by alignment of the molecular axes close to the surface normal, nucleate and grow from this surface liquid. The reaction of these monolayers with ozone was characterized using scanning tunneling microscopy and x-ray photoelectron microscopy; our results show that exposure to ozone results in oxidation of the thiol terminus. The reaction initiates at the c(3x2*3) domain boundary network and propagates into the domains. Above a threshold surface oxygen content, the monolayer converts to a two-dimensional fluid that can subsequently recrystallize to a commensurate monolayer of partially oxidized thiol. Further exposure to ozone results in conversion of the monolayer to a fluid phase and a 10% to 30% expansion of the Au lattice at the Au-thiol interface with concomitant formation of Au islands. Our results demonstrate that crystallographic defects in monolayer films can play an important role in their chemical reactions.

10:20am **SS2+NS+BI+EL-TuM7 Characterization of SAMs with Contrast Variation SPR Technique**, ***K. Tamada***, NIMC and RIKEN Frontier Program, Japan; *H. Akiyama, J. Nagasawa,* NIMC, Japan

We report characteristics of azobenzene-containing self-assembled monolayers (SAMs) which is designed and synthesized for surface photo-isomerization reaction. The surface reaction was monitored by Surface Plasmon Resonance Spectroscopy (SPR), in which the contrast variation technique with various organic solvents was used to improve the accuracy for determination of the optical thickness change by surface reaction. The SAM formation was monitored by kinetic mode experiment with SPR in 0.1mM hexane solution, and after rinsing, refractivity change by UV-VIS photo irradiation was studied in various solvents. In this study, hexyl azobenzene thiol (12-(4-((hexylphenyl)azo)phenoxy)dodecane-1-thiol) SAM was used as an unreactive surface and unsymmetrical azobenzene-disulfides SAMs with the same azobenzene functions were used as reactive ones. Following the previous reports, monomeric dispersion of dye function with disordered chains seems to be necessary to realize highly reactive surface. For our unsymmetrical azobenzene-disulfides SAMs, the free volume for photo-isomerization reaction are guaranteed by 50% dilution of dye functions on surface at monomolecular level. As a result, it was confirmed that unsymmetrical azobenzene-disulfides SAMs were highly reactive, especially, in good solvents (alkanes: C5, C6, C7, C8) and the length of alkyl side chains was quite efficient for surface reactivity.

10:40am **SS2+NS+BI+EL-TuM8 Characterization of a Polymerized Self-Assembled Monolayer Using NEXAFS**, *A.L. Marsh, D.J. Burnett,* University of Michigan; *D.A. Fischer,* National Institute of Standards and Technology; *C.E. Evans,* ***J.L. Gland***, University of Michigan

Near-edge X-ray Absorption Fine Structure, or NEXAFS, at the C-K-edge was used to characterize the orientation of the polymeric backbone in a self-assembled monolayer of 15,9-polydiacetylene. Monolayers were fabricated from the assembly of molecules of dinonacosa-10, 12-diyn-disulfide from a chloroform solution onto a 2000 Angstrom gold film on a mica substrate. Polymerization occurs across one of the C-C triple bonds in the chain, which results in a polymeric network located within the monolayer. Since resonance intensities in NEXAFS spectra are dependent on electric dipole selection rules, it is possible to determine the orientation of the polymeric backbone by comparing spectra at normal incidence (E vector parallel to the surface plane) with spectra at glancing incidence (E vector perpendicular to the surface plane). From the two spectra it was determined that the polymeric backbone is oriented parallel to the surface, while the alkyl chains are oriented perpendicular to the surface. Since NEXAFS probes unfilled molecular orbitals, it is capable of distinguishing between various bonds, i.e. a C-C double bond versus a C-C triple bond, making it possible to determine structural changes as a function of temperature. Upon increasing the temperature, the C-C double bond pi* resonance increases, while the C-C triple bond pi* resonance decreases. These changes would be consistent with a degradation of the polymer backbone. Above a threshold temperature, the changes are irreversible, leading to eventual thermal degradation of the monolayer.

11:00am **SS2+NS+BI+EL-TuM9 An Estimation of Effective Mean Free Path of Photo- and Auger Electrons in Partial Yield Measurements using Self-assembled Monolayers**, ***M. Zharnikov***, *S. Frey, K. Heister, M. Grunze,* Universität Heidelberg, Germany

In the partial electron yield (PEY) acquisition mode commonly used in X-ray absorption spectroscopy both elastically and inelastically scattered electrons contribute to the signal with the latter contribution presumably dominating. In this case a majority of inelastic scattering events will not result in the signal attenuation as it happens in the X-ray photoelectron spectroscopy (XPS). The scattered electrons will still have a kinetic energy in the acquisition range of the spectrometer. The related values of mean free path (MFP) should be, therefore, noticeably larger than the well-known inelastic mean free paths for electrons of definite kinetic energy. We have performed XPS and near edge X-ray absorption fine structure (NEXAFS) spectroscopy measurements for series of self-assembled monolayers of alkanethiols on gold substrate. The length of the alkyl chain and, subsequently, the film thickness was varied. In agreement with the expectations, the obtained effective MFPs for the Au 4f photoelectrons and C@sub KLL@ Auger electrons in the PEY acquisition mode exceed the respective values for the elastically scattered electrons of the same kinetic energies (the Au 4f and C@sub KLL@ electrons made up the elastic component of the acquired PEY signals). Furthermore, the PEY-MFP for the C@sub KLL@ Auger electrons increased with decreasing retarding voltage of the PEY detector, which correlates with the increasing contribution of the inelastically scattered electrons in the acquired signal. The obtained results are of importance for the analysis of NEXAFS spectra in both self-assembled monolayers and polymers. This work has been supported by the German Bundesministerium fuer Bildung, Wissenschaft und Technologie through grant No. 05 SF8VHA 1 and by the Fonds der Chemischen Industrie.

11:20am **SS2+NS+BI+EL-TuM10 Growth Process and Thermal Stability of Semifluorinated Alkanethiol Self-Assembled Monolayers on Au(111)**, ***M. Hara***, Frontier Research System, RIKEN, Japan; *A. Suzuki,* Tokyo Institute of Technology, Japan; *K. Tamada,* National Institute of Materials and Chemistry, Japan; *H. Fukushima,* Seiko Epson Co., Japan; *T.R. Lee,* University of Houston

Growth process and thermal stability of semifluorinated alkanethiol (CF@sub 3@(CF@sub 2@)@sub m@(CH@sub 2@)@sub n@SH) self-assembled monolayers (SAMs) on Au(111) have been investigated by thermal desorption spectroscopy (TDS) and scanning tunneling microscopy (STM). The growth kinetics showed nearly the Langmuir adsorption isotherm and the etch pits were formed in the upright phase, while the striped phases were not observed in the initial growth stage for shorter (CH@sub 2@)@sub n@ semifluorinated SAMs. In TDS, no significant peaks can be obtained for dimer molecules and decomposed species, suggesting no associative desorption nor dimerization and thermal stability of the semifluorinated molecules during heating up to 650 K. Since longer (CH@sub 2@)@sub n@ semifluorinated SAMs remained the same chemisorbed state in the monolayer after annealing at around 480 K, it has been confirmed that also the alkyl chain part plays an important role for the thermal stability and the ordering in the semifluorinated alkanethiol SAMs. Following those results, we propose more detailed surface phase transition model of semifluorinated alkanethiol SAMs in the growth and annealing processes.

11:40am **SS2+NS+BI+EL-TuM11 Multi-technique Study of Self-Assembled AuCN Monolayers on Au(111) Formed by Electrochemical Deposition**, ***T. Yamada***, Waseda University, Japan; *R. Sekine,* Shizuoka University, Japan; *T. Sawaguchi,* AIST/MITI, Japan

Two kinds of monolayers of AuCN electrodeposited on Au(111), indexed (1.15x@sr@3R-30°) and (1.41x2@sr@3R-30°), have been investigated by XPS, UPS and HREELS as well as LEED, AES and STM to determine the geometrical, electronic and vibrational properties. Electrodeposition was performed in an aqueous 1 mM KAu(CN)@sub 2@ solution by applying an electrode potential about 0 - +0.1 V vs SCE on the Au(111) crystal. Sharp LEED patterns were obtained for these two kinds of adlayers. AES indicated that both of these adlayers were composed Au, C and N without impurity. Well ordered adlattices composing domain structures (domain size ca. 10 nm) were observed by STM. XPS yielded Au 4f signals from AuCN indicating small fractional positive charges on the Au atom incorporated in AuCN. The UPS of AuCN/Au(111) was composed of the Au orbitals and weak signals from CN orbitals, assigned by relativistic DV-Xa molecular orbital calculation. The binding energies of CN orbitals are in the order of 4@sigma@ > 5@sigma@ > 1@pi@, which indicates that the C-Au bond is essentially covalent. HREELS yielded vibrational spectra similar to that obtained for AuCN crystalline powder.@footnote 1@ The C-N stretching frequencies were found to be 2140-2160 cm@super -1@, which are consistent with the covalent nature of the C-Au bond. In the frequency region below 300 cm@super -1@, loss peaks related to the Au-N bonds were seen. The (1.15x@sr@3R-30°) adlayer is concluded to be composed of -AuCN- linear chains (polymer chains) that are identical to those embedded in the AuCN crystal. For the (1.41x2@sr@3R-30°) adlayer, HREELS indicated distortion or breaking of Au-N bonds. Some structural models are proposed for this. These results reveal a special inorganic polymeric feature of the self-assembled AuCN adlayers lying parallel along the surface. @FootnoteText@ @footnote 1@G. A. Bowmaker, B. J. Kennedy and J. C. Reid, Inorg. Chem. 37, 3968 (1998).

Surface Science
Room 210 - Session SS3+MC-TuM
Technique Innovations: Experiment, Theory and Simulation

Moderator: S.B. Sinnott, The University of Kentucky

8:20am **SS3+MC-TuM1 Twenty-First Century Modeling: Multiscale Coupling and its Impact on Surface and Interface Science***, **E.A. Carter**,* University of California, Los Angeles **INVITED**

Multiscale modeling is all the rage among computational material scientists in this new century. This refers to a type of simulation which considers phenomena whose length and/or time scales span several - possibly many - orders of magnitude. Examples of such phenomena include, e.g., time scale disparities in surface diffusion and thin film growth, length scale disparities in corrosion-induced cracking of solid materials, etc. In the first example, surface diffusion is "fast" while the flux of material is "slow". In the second example, corrosion involves chemical reactions on the atomic scale while cracking takes place on the meso-to-macroscale. Future materials modeling will account for the complexities across scales. An overview will be given of new techniques being developed that: (i) provide a first principles quantum mechanical description of thousands of atoms (via a linear scaling kinetic energy density functional - KEDF - theory); (ii) couple atomic level interactions, described by KEDF molecular dynamics simulations, to quasi-continuum simulationsof behavior on the micron scale; and (iii) connect first principles quantum mechanics calculations to cohesive zone continuum mechanics simulations of crack propagation in solids. The impact of such coupled simulations on understanding how surface and interface phenomena affect materials behavior on scales beyond the atomic will be emphasized.

9:00am **SS3+MC-TuM3 The KMLYP Density Functional Approximation: A New Method for Accurate Prediction of Activation Barriers and Enthalpies of Reaction***, J.K. Kang, **C.B. Musgrave**,* Stanford University

We develop the KMLYP hybrid DFT method which is shown to predict activation energies and enthalpies of reaction with smaller errors than B3LYP, G2, QCISD(T), CCSD(T), and CBS-APNO. The accuracy of the method is demonstrated on over 100 reactions. The KMLY P exchange functional is a hybrid functional that combines Hartree-Fock exact exchange with Slater exchange. The correlation functional is a hybrid functional combining Lee-Yang-Parr (LYP) correlation and Vosko-Wilk-Nusair (VWN) correlation. For reactions with reliable experimental data, the RMS deviation of the activation energies are 0.64 kcal/mol, 1.59 kcal/mol, 3.20 kcal/mol, and 3.10 kcal/mol for the KMLYP, CBS-APNO, G2, and B3LYP methods, respectively. The RMS deviations from experiment of the entha lpy of reaction are 1.57 kcal/mol, 2.24 kcal/mol, and 2.87 kcal/mol for the KMLYP, G2 and B3LYP methods, respectively. The KMLYP maximum absolute deviation of the activation barriers is 1.2 kcal/mol while the KMLYP maximum absolute deviation of the enthalpy of reactions is 3.8 kcal/mol. Furthermore, KMLYP is significantly more efficient than the G2, QCISD(T), CCSD(T), and CBS-APNO methods and is practical for the simulation of surface reactions using relatively large clusters.

9:20am **SS3+MC-TuM4 Probing Chemical Interactions at the Single Bond Level***, **M.K. Weldon**,* Bell Laboratories, Lucent Technologies*; J.D. Batteas,* City University of New York, College of Staten Island*; K. Raghavachari,* Bell Laboratories, Lucent Technologies

The measurement of chemical bond strengths is a fundamental goal of much of chemistry; indeed the making and breaking of bonds between atoms is the essence of chemical science. Despite this, the direct measurement of bond strengths has remained an elusive goal due primarily to the inherent difficulty in localizing the requisite excitation along a single bond coordinate. Here we demonstrate a methodology for measuring the strength of individual chemical bonds at solid surfaces. We have used atomic force microscopy (AFM) to probe the pH-dependent changes in the surface chemistry of silica in the single bond limit. We observe quantized adhesion forces that, when referenced to the results of ab initio quantum chemical cluster calculations, can be unambiguously assigned to single neutral hydrogen bonds (OH..OH), single ionic hydrogen bonds (OH@super -@..OH) and single covalent bonds (Si-O-Si) between the tip and surface. We have subsequently extended this work to measure the interaction (bond) energetics in a number of aqueous and organic solvent systems. Remarkably, we find that we able to observe individual H@sub 2@O..H@sub 2@O hydrogen bonds under the appropriate conditions, as well as the attendant isotopic shift and bond weakening upon raising the temperature, again demonstrating the potential of this approach for exploring the nature of chemical bonds in solution. In summary, this breakthrough in chemical analysis is predicted to be generalizable to all solution reactions for which the constituent reagents can be chemically functionalized onto a solid surface. To this end, we are currently investigating the interaction energetics in a variety of reactive organic systems.

9:40am **SS3+MC-TuM5 Surface Vibrational Spectroscopy Beyond the Harmonic Approximation, Experiments and Calculations***, **P. Uvdal**, M.P. Andersson, R. Asmundsson,* Lund University, Sweden*; A.D. MacKerell, Jr.,* University of Maryland

Vibrational analysis of surface adsorbates involves in general the assignment of fundamental normal modes. Based on such assignment conclusions about chemical identity and geometry can be drawn. It is however well known from fundamental textbooks on molecular vibrations that if one goes beyond the harmonic approximation of the intramolecular bond potential overtone and combination modes are allowed. Binary modes, i.e. excitation of one vibration with two quanta or excitation of two vibrations with one quanta, will be the most intense even though higher excitations are allowed. The presence or absence of binary modes will contain information about bond anharmonicity and coupling between different modes. The latter may reveal surface induced changes of activation barriers of importance for the understanding of e.g. heterogeneous catalysis. The former reveal dynamical properties of the system as the extent of coupling governs the dissipation and randomization, within the molecule, of the energy initially localized in a single bond excitation. Using methoxy and ethoxy adsorbed on Cu(100) and W(110) surfaces as model systems we will demonstrate binary intramolecular modes in the presence and absence of Fermi resonance coupling. We will also show a combination mode consisting of the C-O stretch and the hindered motion of methoxy with respect to the surface.

10:00am **SS3+MC-TuM6 Time Resolved Fourier Transform Infrared Spectroscopy***, **M. Kovar**, P.R. Norton,* University of Western Ontario, Canada

We have developed a data acquisition system based on digital signal processing for a broadband time-resolved Fourier Transform Infrared Spectrometer. In FTIRS, broadband infrared radiation is modulated by means of a Michelson interferometer. The position of the moving mirror is tracked by the fringe pattern of a reference He/Ne laser, whose beam follows the same optical path as the infrared radiation. Pulses used for time resolution as fast as 500 ns are modulated on a reference He/Ne laser signal. We have chosen a slower mirror speed which permits observation of an external perturbation of a system under investigation which often limits the mirror speed. Different external perturbations can be used, such as thermal, mechanical, photochemical or those caused by external potential. We discuss characteristics of time resolved FTIRS and its performance. The system will permit grazing incidence IR reflection-absorption measurements of surface and thin film processes with sub-microsecond time resolution.

10:20am **SS3+MC-TuM7 Momentum Space Line Narrowing by Angle Resolved Auger-photoelectron Coincidence Spectroscopy***, A. Danese, **R.A. Bartynski**,* Rutgers University*; R. Gotter,* Lab. Nazionale TASC-INFM, Trieste, Italy*; S. Iacobucci,* CNR-IMAI Montelibretti, Italy*; G. Stefani,* U. di Roma III, Italy

We have measured the Ag N@sub 23@VV Auger electron diffraction pattern from the Ag(100) surface in coincidence with Ag 4p photoelectrons under high energy and angular resolution conditions. Measurements were performed using the ALOISA beamline at the ELETTRA synchrotron in Trieste. It is well known that the Auger and photoemission spectra associated with the shallow 4p (3p) core levels of the late 4d (3d) transition metals are unusually broad in energy owing to the rapid decay of the core hole. Furthermore, it has been shown for the Cu 3p and Ag 4p levels that this energy broadening can be eliminated in Auger-photoelectron coincidence (APEC) energy distribution curves. However, this lifetime broadening is expected to generate a concomitant momentum broadening and the resultant Auger diffraction pattern has only a very weak intensity modulation of ~15%. By performing an APEC measurement with high energy and angular resolution, this momentum broadening should be eliminated. In our APEC angular distribution curves, intensity modulations are enhanced to ~50%, consistent with a significant reduction of the momentum uncertainty of the outgoing Auger electrons. These results provide direct evidence that the photoexcitation/Auger decay of these levels is a coherent process. The implications of these results in the context of Auger electron diffraction will be discussed.@footnote 1@ @FootnoteText@ @footnote 1@ Supported by NSF grant NSF-DMR9801681 and NATO grant CRG97-0175.

10:40am **SS3+MC-TuM8 A Microarray Technique for Measuring Adsorption/Desorption Kinetics***, **M.C. Wheeler**, R.E. Cavicchi, G.E. Poirier, S. Semancik,* National Institute of Standards and Technology

We have developed a novel method for characterizing the kinetics and thermodynamics of adsorption and desorption that uses a 340-element array of micromachined Si hotplates as the sample platform. The method takes advantage of the microhotplates' rapid heating characteristics (10@super 6@ °C/s), intermediate between traditional temperature programmed desorption methods and pulsed laser desorption. The method is isobaric, particularly useful for studying many systems where the desorption rate is significant at room temperature, and readily automated to efficiently produce large data sets for adsorption systems. Under constant gas exposure, all of the array elements are simultaneously subjected to square temperature pulses as short as 5 ms. An example sequence is a high-T cleaning pulse (as high as 800 °C), a low-T adsorption pulse, an intermediate-T desorption pulse, and a final high-T cleaning pulse. Variation of the pulse amplitude and duration allows determination of the adsorption and desorption rate constants and energies. Signal-to-noise is enhanced by using a large array of microhotplate devices and averaging of repeated pulse sequences. The pressure range is extended to over 10@super -5@ Torr using a differentially pumped mass spectrometer system (even higher effective pressures can be achieved with a directed doser). We illustrate the technique by mapping adsorption isotherms and extracting parameters for methanol on CVD-deposited SnO@sub 2@ polycrystalline films, such as are used in gas sensing; however, wide ranges of materials and adsorbates can be investigated with this technique. In addition to emphasizing the convenience, flexibility, simplicity, and efficiency of this automated technique, we will also discuss challenges that we have had to address - the most significant relating to temperature calibration and uniformity.

11:00am **SS3+MC-TuM9 Scanning Probe Energy Loss Spectroscopy: Spectroscopic Analysis of Reflected Electrons in Field Emission STM***, **B.J. Eves**,* University of Birmingham, UK*; F. Festy, K. Svensson,* University of Birmingham, UK, U.K.*; R.E. Palmer,* University of Birmingham, UK

Spectroscopic (i.e. chemical) analysis is a key frontier in scanning probe microscopy. We have employed a scanning tunnelling microscope (STM) operating in field emission mode to act as a nanometre scale electron source while the resulting backscattered electrons have been detected with a hemispherical energy analyser. Angular measurements show that the flux of reflected electrons peaks parallel to the surface, consistent with simulations which include the long range field generated by the tip bias voltage. The measured energy loss spectra contain information on the surface and bulk plasmons, and other surface excitations. The Si (111)-7x7 surface was found to show losses at 5, 7.5, 11, 15, and 18 eV. These inelastic losses correspond to an interband transition (5 eV), two surface states (7.5 and 15 eV), and the surface and bulk plasmons (11 and 18 eV, respectively). Spectra have also been measured for a number of different exit angles. With improvements it is believed that the scanning probe energy loss spectrometer (SPELS) can be built to perform electron energy loss spectroscopy with spatial resolution on the scale of 5-50 nm.

11:20am **SS3+MC-TuM10 Application of a Direct Method in Surface X-ray Crystallography***, **P.F. Lyman**, R. Harder, D.K. Saldin,* University of Wisconsin, Milwaukee*; C.-Y. Kim, K.W. Evans-Lutterodt,* Lucent Technologies

The electron density of the near-surface region of a crystal could be recovered from x-ray scattering data if the phases of the scattered radiation were known. In the case of surface scattering, the diffracted intensities arise from the square of a linear combination of bulk and surface amplitudes. Since the phases and amplitudes of the bulk component can be calculated accurately, it is possible to use the bulk scattering as a reference wave, and to thereby estimate the phases of the surface component, in analogy with holography. We have developed an algorithm to estimate the most likely set of surface phases, and to thereby recover the electron density of the near-surface region. We present preliminary applications of this method to (2x1)-reconstructed Ge(001) surfaces. It has been shown that the (001) face of Ge or Si can be passivated by 1 ML of a group V element. Although there is general acceptance of the existence of symmetric group V dimers for most adsorbate/substrate combinations, a controversial result of asymmetric Sb dimers for the Sb/Ge(001) system was concluded from an x-ray scattering study: Each Sb dimer was found to have shifted along the axis of the Sb-Sb bond.@footnote 1@ However, a number of first-principles calculations have found no evidence for the shift. We will use our direct reconstruction algorithm on experimental x-ray scattering data to address the possibility of shifted dimers in a model-independent way. @FootnoteText@ @footnote 1@ M. Lohmeier, H.A. van der Vegt, R.G. van Silfhout, E. Vlieg, J.M.C. Thornton, J.E. Macdonald and P.M.L.O. Scholte, Surf. Sci. V. 275, p.190 (1992).

11:40am **SS3+MC-TuM11 Line of Sight Techniques: Providing an Inventory of all Species Arriving at and Departing from a Surface***, **R.G. Jones**,* University of Nottingham, UK, U.K.*; A.S.Y. Chan, M.P. Skegg,* University of Nottingham, UK

Line of sight techniques comprise those methods in which species emanating from a surface (atoms, molecules and radicals) undergo just a single pass through the ionisation volume of a mass spectrometer before being pumped. This is achieved by enclosing the mass spectrometer within a cryoshield fitted with appropriate apertures, such that line of sight is established only between a patch on the sample surface (ca 7 mm diameter) and the ionisation volume. All LOS techniques are inherently angle resolved, free from extraneous signals and have approximately equal detection probabilities for all species. Line of sight temperature programmed desorption (LOSTPD)@footnote1@ is a particularly reliable way of obtaining TPD data. By applying an over pressure of gas to the sample and monitoring the reflected flux, we get line of sight sticking probability (LOSSP) measurements@footnote 2@ giving S to an accuracy of 0.02; while monitoring of the reaction products at constant temperature gives line of sight product desorption (LOSPD) data. These techniques provide new, powerful and reliable ways of studying all aspects of surface kinetics, by allowing an inventory of all species arriving at and departing from a surface, for any combination of partial pressures, surface temperature, surface composition and surface structure. In this paper we illustrate these methods using the reactions of 1-bromo-2-chloroethane (BCE) and ioodotrifluoromethane with Cu(111). For BCE we show that it undergoes non-activated dissociative adsorption with a transition state 13 kJ/mol below zero (0 = molecule at infinity). For CF@sub3@I we observe emission of CF@sub3@ radicals and coupling reactions forming, among others, C@sub2@F@sub4@. @FootnoteText@ @footnote 1@ R.G. Jones and S. Turton, Surface Sci. 377-379 (1997) 719. @footnote 2@ R.G. Jones and C. J. Fisher, Surface Sci. 424 (1999) 127.

Thin Films

Room 203 - Session TF-TuM

Thin Films in the 21st Century

Moderator: G.N. Parsons, North Carolina State University

8:20am **TF-TuM1 Atomic-Level Control of Microstructure, Morphological Evolution, and Physical Properties during Film Growth: The Golden Era of Materials Science***, **J.E. Greene**,* University of Illinois, Urbana **INVITED**

A primary goal of research being carried out worldwide in the area of thin film crystal growth from the vapor phase is the development of the ability to understand, control, and quantitatively model - at the atomic scale - surface chemical reaction pathways, growth kinetics, and microstructural evolution. This typically involves operating far from thermodynamic equilibrium in order to selectively open new kinetically-limited reaction paths and has resulted in the development of hybrid growth techniques which combine the inherent advantages of CVD (choice of precursor chemistries for site-specific surface reactions, self-limiting surface terminations, surface-mediated reaction kinetics, surfactant reactions, and conformal coverage), MBE (clean UHV processing compatible with in-situ surface science techniques, and low deposition temperatures), and sputter deposition (the use of hyperthermal particles to overcome surface kinetic barriers). In-situ structural (e.g., RHEED, LEED, STM, AFM) and chemical (e.g., AES, XPS, EELS, STS, TPD) probes coupled with powerful post-deposition analytical techniques such as high-resolution TEM and synchrotron-XRD, RBS, SIMS, and PL have provided the primary tools for rapid experimental progress over the past few years. The corresponding development of efficient computational methods for molecular dynamics, kinetic Monte Carlo, and density functional theory, together with powerful analytical approaches such as level-set schemes which easily handle singularities and higher dimensions, allows robust predictive modeling to proceed in parallel with experiment. Examples of atomic-scale manipulation of film chemistry, surface morphology, epitaxy by driven assembly, and preferred orientation in polycrystalline layers will be discussed. Structure and chemistry can be manipulated at all length scales from nanometer to mesoscopic to continuum through increasingly complex organizational hierarchies.

9:00am **TF-TuM3 1D Nanostructures: Building Blocks for Nanotechnologies*, C.M. Lieber,*** Harvard University **INVITED**

One-dimensional (1D) nanostructures, such as nanowires and nanotubes, are critical building blocks that have the potential to impact many emerging and proposed areas of nanoscale science and technology. This presentation will focus on exploiting our fundamental understanding of growth and physical properties of these nanoscale materials to design and assemble rationally functional nanoscale tools and devices. First, the orthogonal assembly of semiconductor nanowires into integrated multi-terminal electronic and optoelectronic devices and the resulting properties of these structures will be described. Second, a new concept for a carbon nanotube based molecular scale computer will be discussed together with proof of concept experiments. Third, critical tools for imaging, sensing and manipulation at the single molecule scale, which are based on the unique mechanical and electromechanical properties of nanotubes, will be discussed.

9:40am **TF-TuM5 Challenges for Thin Films in Communications*, W.D. Westwood,*** THINK Films, Canada, Ontario **INVITED**

Considering the growth rate in both the demand for thin films and the capability to fabricate them over the past 40 years, it is a daunting task to predict the future of thin film technology, even over the next decade. Apart from Zn evaporation for paper capacitors, the main application of thin films for telecommunications prior to 1960 were electroplated Au relay contacts. Sputtering Ta based resistors and capacitors for tone touch telephone frequency generators was the first of a new range of applicatio ns. Today, there are many very demanding applications in integrated circuits and optical components for communication systems; e.g wavelength separation in high speed fiber systems utilizes over 100 oxide layers in interference coatings with a precision of better than 0.1%. The number of deposition methods has greatly increased in the past 40 years; a whole range of techniques involving combinations of physical, chemical and plasma processes are now used to deposit films for specialized applications. In parallel, sophisticated analytical techniques have provided better understanding of the composition and structure of films and the growth processes. Despite these advances, the requirements for control of films remains ahead of the capability and even better methods are required. Will improvements in PVD or CVD methods meet the requirements or will new techniques provide the high yield, high precision processes which are required?

10:20am **TF-TuM7 The Transition from Thermally-grown SiO@sub 2@ to Deposited Thin Film Alternative Gate Dielectrics*, G. Lucovsky,*** North Carolina State University **INVITED**

This continued scaling of lateral dimensions of Si field effect transistors to increase device packing densities, and to improve high frequency performance requires proportional decreases in the effective thickness of the gate dielectric. When this equivalent oxide thickness, EOT, is reduced to < 2.5 to 3 nm, direct tunneling emerges as an important factor in device performance and reliability. Direct tunneling at bias voltages for channel inversion exceeds 1A-cm-2 at EOT ~1.5 to1.6 nm, and defines a limitation for thermally-grown SiO@sub 2@ for high power devices. Limitations for portable devices are much more restrictive. The obvious solution for extending EOT to significantly smaller values ~0.5-0.6 nm is to introduce deposited thin film alternative gate dielectrics with higher dielectric constants. This is a formidable task, since the performance and reliability of devices with thermally-grown SiO@sub 2@ derives from i) the low density of defects, trapping sites and fixed charge, at the Si-SiO@sub 2@ interface, and the ii) the low density of electrically-active defects in the SiO@sub 2@ film. Deposited gate dielectrics will then require separate and independent control of the properties of Si-dielectric interface, and the thin film alternative dielectric generally in stacked configurations. Introduction of alternative gate dielectrics will proceed in two steps, i) replacement of SiO@sub 2@ with deposited silicon oxynitride alloys and silicon nitride, extending EOT to ~ 1.1 nm, and then iii) replacement of the dielectrics of i) with metal-oxide and silicate thin films with dielectrics constants in excess of 10. This paper will address issues relevant to single layer and composite structures for both groups of replacement dielectrics identified above.

11:00am **TF-TuM9 Porous Coatings with Engineered Microstructure*, M.J. Brett,*** University of Alberta, Canada **INVITED**

Traditional thin film coatings are often optimized for durability, density and uniformity. However, recent opportunities for porous thin films have led to development of new techniques for fabrication of extremely porous coatings with precisely controlled microstructure. One such process is Glancing Angle deposition (GLAD), which combines the features of glancing incidence flux at the substrate with controlled substrate motion. Whereas "normal" evaporated or sputtered thin films usually possess a columnar structure that is densely packed, in the GLAD process extreme self shadowing from nuclei leads to greatly increased separation of columns and growth of isolated microstuctures. Microstructural shape may be tailored by substrate motion to produce, for example, helices, pillars, chevrons, and S-curves with feature sizes from 10 nm to 20 µm. In this manner GLAD has been utilized for simple one-step fabrication of films of high surface area and controlled porosity and structure from dielectric, semiconductor, metal, and alloy materials by sputtering, evaporation, and pulsed laser deposition. Although the stochastic nature of the deposition normally leads to random column nucleation, large area periodically arranged micropost or microhelix arrays may be easily created by deposition over patterned seeds on the substrate. This talk will present details of oblique deposition processes, characterization and description of film microstructures, and results of investigations or of opportunities for the use of engineered porous films in optics, thermal barriers, sensors, magnetics, and as high surface area devices.

11:40am **TF-TuM11 Thin Film Technology in the 21st Century*, F. Jansen,*** BOC Edwards **INVITED**

A century of technology development and materials engineering has provided us with deposition processes for nearly every imaginable material. Interactions between process parameters and materials properties are generally well understood. Today, this allows the controlled deposition and crafting of complicated devices of which thin-ness and small-ness is a fundamental attribute. As the technology of thin films progressed from optical to electronic applications, the definition of 'thin' moved from the 100 nm scale into the <10 nm domain where atomic scale effects start to become important design considerations. The opening of the 21st century brings us to a convergence of thin film deposition with atomic scale engineering. Atomic layer deposition is aimed at nanoscale process control. Self-assembled monolayers provide surfaces with unique and useful properties. Microelectronic mechanical sensors require a broad spectrum of nanoscale engineered materials all based on thin film techniques. Approaching device applications from the opposite direction of the thickness scale, will challenge the thin film technologist to develop new methods to control the process and achieve practicality. The shift from inorganic to organic electronic materials is predicted to continue with concomitant changes in process technology. With microelectronics now reaching fundamental limits of miniaturization, thin film technologists will be forced to return to their beginnings, optical device technology, be it this time on a scale and with a required degree of control that was unthinkable in the last century.

Biomaterial Interfaces
Room 202 - Session BI+EL-TuA

Cell-Surface Interactions

Moderator: D.W. Grainger, Colorado State University

2:00pm **BI+EL-TuA1 Model Surfaces for Studying and Controlling the Adhesion of Cells*, M. Mrksich,*** The University of Chicago **INVITED**

This presentation will give an overview of the use of self-assembled monolayers of alkanethiolates on gold as model substrates for studying and controlling the interactions of cells with non-natural materials. This surface chemistry approach begins with monolayers terminated in short oligomers of the ethylene glycol group, because these films are inert to the non-specific adsorption of protein. Monolayers patterned into regions presenting glycol groups with the complementary regions presenting hydrophobic surfaces are excellent substrates for patterning the attachment of cells. The immobilization of ligands to these inert films gives substrates to which proteins can selectively bind, but which otherwise rule out non-specific interactions of proteins. This approach can be extended to give substrates that mediate the attachment of mammalian cells. Monolayers presenting the peptide Arg-Gly-Asp (a ligand for cell-surface integrin receptors) mediate the selective attachment and spreading of fibroblast cells. This presentation will also discuss the design of dynamic substrates that can alter, in real time, the presentation of ligands to an attached cell and hence influence the behaviors of adherent cells. These active substrates are based on electroactive monolayers that present redox-active groups which can be switched by applying electrical potentials to the underlying gold. A first example uses substrates that can be switched to turn on the immobilization of ligands. This strategy has been used to switch regions of the substrate from an inert state to a state that permits the adhesion and migration of cells. A second example uses substrates that can selectively release immobilized ligands from the monolayer. These examples establish that self-assembled monolayers of alkanethiolates on gold are an excellent model system for controlling the adhesion of cells and will find wide use both in fundamental studies for biology and in applied targets for biotechnology.

2:40pm **BI+EL-TuA3 Cell Respone to Chemically and Topographically Modified Surfaces*, D.S. Sutherland,*** *A.S. Andersson, K. Glasmastar, S. Petronis,* Chalmers University of Technology, Sweden*; F. Backhed, A. Richter-Dahlfors,* Karolinska Institute, Sweden*; U. Lidberg,* University of Gothenburg, Sweden*; B. Kasemo,* Chalmers University of Technology, Sweden

The properties of surfaces have long been known to influence cellular behaviour. Both the chemistry and topography of surfaces have been shown to effect different aspects of cellular response. With the advent of micro and nanofabrication it is now possibl e to study these interaction in a more detailed fashion, isolating specific surface structures and systematically varying their size and shape. In a parallel multicentre project a range of micro and nanofabricated surfaces are used in cell culture experi ments with a range of cell types. The specific surface designs were selected to give chemical and topographic cues on a range of length scales from the micron and submicron to the nanometre and were used as a set, to screen for the influence of surface st ructure on cellular behaviour. Similar sets of well-characterised surfaces were used in a number of different cell culture systems, including epithelial, endothelial, mammary gland and pancreatic cells, to look for both cell-specific interactions and g ene ric correlations. The studies have taken advantage of recent advances in microbiological techniques, focussing on different aspects of gene expression, cell differentiation and cell-cell signalling as well as more traditional adhesion, proliferation and m orphologic analysis. Examples of preliminary results obtained so far include: 1. Non-adherence/proliferation of three cell types to lipid bilayers (so called supported membranes) 2. Expression of a specific cytokine by epithelial cells is influenced by the microtopography of the surface. Additional results from ongoing studies are expected within a few months.

3:00pm **BI+EL-TuA4 Directing Endothelial Cell Attachment and Growth Using a Novel Ozone Patterning Technique**, *S.R. Webb, **T. Boland,*** Clemson University

Being able to modify surfaces to control cellular behavior, i.e. adhesion, spreading, migration, and or proliferation is extremely important in the development of materials for tissue engineering applications. Of particular interest in the field of vascular research are surfaces that will direct cell attachment and growth in the presence of RGD containing serum proteins, which may adsorb to the material surface. In this study, cell response to patterned materials was examined by employing highly organized monolayers of self-assembled (SAM) octadecytrichlorosilane (OTS) on silicon oxide wafers. OTS surfaces were exposed to ozone for a varying amount of time ranging from 1-4 minutes. The remaining surfaces were exposed to ozone via a micron size mask, allowing only the exposed areas to be etched. The surfaces were analyzed by ellipsometry and electron spectroscopy for chemical analysis (ESCA). Bovine aortic endothelial cells (BAEC): were cultured in MEM + 10% Fetal Bovine Serum + 1% antibiotic solution. Cells were seeded and cultured in 96 well plates in the presence of pure and patterned OTS surfaces. Cell attachment and growth of endothelial cells on pure OTS monolayers was very poor, most likely because of the denaturing of serum proteins near the surfaces. The surfaces exposed to ozone showed varying film thickness depending on the dose, and a strong carbonyl peak in the ESCA spectra, indicating the presence of an oxidized thin organic film. Cell attachment to etched surfaces and growth exceeded the control tissue culture polystyrene. Cell density increased in regions of the pattern to a confluent layer. The cell spreading and attachment on the micro-patterned surfaces suggests that the cells may be able to attach more firmly to the extracellular proteins on the patterned surfaces. The result from this cell growth study will aid in designing micro-patterned surfaces varies areas, such as, cell-based biosensors, biocomputers, and new biomaterials.

3:20pm **BI+EL-TuA5 Cellular Interactions with Self-assembled Monolayers*, G.J. Leggett,*** University of Manchester Institute of Science and Technology, UK **INVITED**

The development of a detailed understanding of the influence of surface chemical structure on mammalian cell attachment has been confronted with difficulties. Not only are the biological problems inherently complex, but until recently there have not been adequately well defined model surfaces for fundamental studies. The advent of self-assembled monolayers (SAMs) has promised to transform this situation, by providing well-defined surfaces with structures and chemistries that may readily be controlled, and the past five years have seen growing interest in the use of SAMs to model cellular interactions with artificial substrata. In the present work, SAMs with a range of alkyl chain lengths and terminal groups have been used in studies of the attachment of murine 3T3 fibroblasts and primary human osteoblast-like cells. The sensitivity of cellular attachment to subtle changes in adsorbate molecular structure and order has been explored. The responses of cells to micropatterned substrata formed using photopatterning methods have been explored. The organisation of structural elements, including filamentous actin organisation and focal contact formation, within the cell cytoskeleton has been explored using immunochemical methods. The effect of protein adsorption has been probed by comparing attachment from serum-free and full media, and by pre-exposing surfaces to protein solutions. Valuable insights have been gathered into the relationship between surface chemical structure and cellular behaviour.

4:00pm **BI+EL-TuA7 Artificial Networks of Rat Hippocampal Neurons on Microelectrode Arrays*, C.D. James,*** *A.J. Spence,* Cornell University*; N. Dowell,* Wadsworth Center/Department of Health*; H.G. Craighead, M.S. Isaacson,* Cornell University*; J. Turner, W. Shain,* Wadsworth Center/Department of Health

The construction of artificial neuronal networks from dissociated primary neurons will permit study of synaptogenesis, synaptic plasticity, and neuronal processing. However, a thorough investigation of these processes requires two important components: a flexible method of producing patterned cell networks, and long-term (weeks) studies of such cell networks. To address these issues, microelectrode arrays have been fabricated to conduct long-term, non-invasive extracellular measurements of spontaneous and induced action potentials. In addition, we have used two methods, microcontact printing and conventional photolithography, to align patterns of molecules, such as poly-L-lysine and laminin, to the microelectrode arrays. Surface analysis of the patterned molecules was completed to assess the relevant factors for successfully promoting cell attachment and neurite guidance. Issues dealing with the reliability and stability of the microfabricated electrode arrays, specifically for primary neuron cell cultures, will also be addressed.

4:20pm **BI+EL-TuA8 Living Neural Cells as Components in Sensors and Computational Devices*, J.J. Hickman,*** Clemson University **INVITED**

We are developing the methodology to build hybrid biological/non-biological systems to create new information technology devices. This presentation will focus, from a bioengineering standpoint, the steps necessary to build such a device and some of the possible functions of these devices. We are using self-assembled monolayers (SAMs) to control the intrinsic and geometric properties of surfaces in contact with biological systems. The use of surface modification techniques allows us to tailor the interface between biological/nonbiological materials independent of the bulk composition of the nonbiological material. The ability to control the surface composition of the in vitro system as well as controlling other variables, such as growth media and cell preparation, all play important roles in creating a defined system for devise operation. This defined system has been used as a test-bed to evaluate surface coatings for neuronal interactions with electronic materials. We have used the geometric control of the surface composition afforded us by SAMs to create in vitro circuits of mammalian neurons. We have also recorded the electrophysiological signals produced by neurons on the patterned SAMs in response to stimuli. The surfaces have been characterized by X-ray photoelectron spectroscopy (XPS), imaging XPS and contact angle measurements and we have related the intrinsic properties of the surface and the proteins deposited by the cells to cellular development. We are using what we learn for a more fundamental understanding of cellular development and also to create sensors using living neurons as the sensor element. The continuing development of this technology will be discussed, our latest results, as well as the implications and applications for (a) biosensor fabrication, (b) neuronal circuit design, and (c) biological computation.

5:00pm **BI+EL-TuA10 Tissue Formation of Hepatocytes on Micro-Porous Films of Polylactide***, **T. Nishikawa,*** RIKEN, Japan*; K. Nishikawa, R. Ookura, J. Nishida, S.-I. Nishimura, H. Ookubo, H. Kamachi, M. Matsushita, S. Todo,* Hokkaido University, Japan*; M. Shimomura,* RIKEN, Japan

Control of interaction between cells and material surfaces has been considered as a fundamental issue in designing and developing bio-materials for various purposes such as cell culture, implantation, and tissue regeneration. Surface morphology is one of the factors which can control the interaction. We previously reported that two-dimensional regular honeycomb pattern appear as a surface morphology of polymer films which were fabricated by casting dilute solution of amphiphilic polymers on solid substrates in a humid atmosphere. Recently we found that the honeycomb morphology can be applied to micro-patterning of cell culture substrates and that rat hepatocytes recognize the micro-patterned surfaces from chemical and morphological aspects and change their morphology and functions. Here we show that self-supported honeycomb films can be fabricated by casting a dilute solution containing polylactide (PLLA) as major component of the films and amphiphilic polymer as component for induction of honeycomb morphology. The honeycomb films worked as cell culture substrates for rat hepatocytes. Hepatocytes on the honeycomb films formed a colony, which exhibited tissue-like structure and express high level of albumin secretion, which was comparable to that of spheroids of hepatocytes. The tissue formation of hepatocytes specifically occurred on the honeycomb films of PLLA, but not on flat films of PLLA. The colony of hepatocytes kept the morphological features and liver specific function at day 14. This indicates that micro-porous films of PLLA would be appropriate for long term culturing of hepatocytes. Recently we succeeded in culturing hepatocytes on both sides of the self-supported honeycomb films of PLLA. In this sense, we believe that our materials possessing regular micro-pores are applicable to artificial extra-cellular matrices for tissue engineering.

Electronics
Room 312 - Session EL+NS-TuA
Nanoelectronics

Moderator: R.S. Goldman, University of Michigan

2:00pm **EL+NS-TuA1 Nano-switches Using Vacuum Nano-electronics and Superconducting Weak Links***, **D.G. Hasko,*** Cambridge University, UK **INVITED**

New physical principles influence device operation when size is reduced to the nanometre range Recent research has lead to two types of switching devices; vacuum nanoelectronic (VNE) and superconducting switches have been described and are reviewed in this paper. Conventional vacuum microelectronics exploits cold field emission of electrons in devices made by microcircuit fabrication techniques but requires UHV vacuum operating conditions. By reducing the field emission tip radius and the tip-extractor electrode spacing a new class of VNE devices may be operated at lower voltages and with improved stability. Tips of nanometre size also show much smaller angular spreads and reduced energy spread. Diode and triode devices, with electron transport path length of ~100nm (shorter than the mean free path in air) were fabricated and their electrical characteristics reported. Hot phonon injection from an electrically isolated heater has demonstrated effective switching behaviour in Nb weak link junctions and is of great interest for high speed and quantum effect circuit functions. This method isolates the control circuit from the weak link and has demonstrated significant device gain in contrast to previous device structures.

2:40pm **EL+NS-TuA3 Persistent-current Qubits for Quantum Computation***, **E.L. Mooij**,* DIMES Institute, The Netherlands **INVITED**

In a collaboration between MIT and Delft University we have designed a quantum bit (qubit) for quantum computation that consists of a superconducting loop with three small Josephson junctions in series.@footnote 1@ When the flux through the loop is close to half a superconducting flux quantum, the qubit has two stable macroscopic quantum states with persistent currents in opposite directions. Quantum transitions between the two states are possible if the capacitance of the junctions is small. Samples are fabricated from aluminum and measurements are performed at very low temperatures to reduce decoherence effects. First measurement results have been obtained that demonstrate the quantum superposition of the states. Next experiments will focus on time-dependent response. With these qubits in principle a scalable quantum computer can be constructed if the decoherence time is long enough. A quantum computer of sufficient size can perform calculations beyond the power of a conventional computer. However, many challenges will have to be faced before a quantum computer is realized. @FootnoteText@ @footnote 1@J.E. Mooij, T.P. Orlando, L.Levitov, Lin Tian, Caspar H. van der Wal and Seth Lloyd, Science 285, 1036 (1999)

3:20pm **EL+NS-TuA5 Coulomb Blockade Devices Fabricated by AFM-manipulation of Nanoparticles***, S. Carlsson, T. Junno, H. Xu,* ***L. Samuelson**,* Lund University, Sweden

We report successful fabrication of Coulomb blockade devices obtained by manipulation of pre-fabricated nanoparticles, using an atomic force microscope (AFM) as a nano-engineering tool. This approach, together with in-situ electrical measurements during manipulation, allows the formation of tunnel gaps with accuracy on the Ångstrom scale. Three-terminal single-electron transistors (SETs) with ideal electrical characteristics are obtained, demonstrating Coulomb blockade as well as Coulomb staircase in the I-V characteristics, and with hundreds of current oscillations as function of gate voltage. Furthermore, we have built double-island structures with three gaps trimmed to tunneling dimensions and with two addressing gates, allowing control of the charge distribution, or polarization, of these two-atom artificial molecule objects.

3:40pm **EL+NS-TuA6 A Novel Scheme for the Fabrication of Ultra-short Metal-oxide-semiconductor Field-effect Transistors***, **R. Martel,*** IBM T.J. Watson Research Center*; J. Appenzeller, J. Knoch,* Physikalisches Institut, RWTH Aachen, Germany*; K. Chan,* IBM T.J. Watson Research Center*; M. Tanner, S. Thomas, K.L. Wang,* University of California, Los Angeles*; Ph. Avouris,* IBM T.J. Watson Research Center*; J.A. del Alamo,* Massachusetts Institute of Technology*; P. Solomon,* IBM T.J. Watson Research Center

We present a novel scheme for the fabrication of ultra-short channel length metal-oxide-semiconductor field-effect transistors (MOSFETs) involving nanolithography (proximal probe or e-beam) and molecular beam epitaxy (MBE). The active channel is undoped and is defined by a combination of nanometer-scale patterning and anisotropic etching of a n@super ++@-layer grown on a silicon on insulator (SOI) wafer. The method is self-limiting and can produce MOSFET devices with channel lengths of less than 10nm. Measurements on the first batches of n-MOSFET devices fabricated with this new approach will be presented. They show very good output characteristics and good control of the short channel effects. The combination of highly doped contact areas (n@super ++@ 1x10@super 20@cm@super -3@) with a nominally undoped channel region (p@super -@ 5x10@super 14@cm@super -3@) is now being explored further to keep the parasitic resistances low and possibly achieve ballistic transport at room temperature.

4:00pm **EL+NS-TuA7 Quantitative Analysis of Charge Injection and Discharging of Si Nanocrystals and Arrays by Electrostatic Force Microscopy***, **L.D. Bell,*** Jet Propulsion Laboratory, Caltech*; E. Boer, M. Ostraat,* Caltech*; M.L. Brongersma,* Caltech, US*; R.C. Flagan, H.A. Atwater,* Caltech

Charge injection and storage in dense arrays of silicon nanocrystals in SiO@sub 2@ is a critical aspect of the performance of potential nanocrystal flash memory structures. We have performed charging experiments on Si nanocrystals both embedded within and deposited on SiO@sub 2@ using conducting-tip atomic force microscopy (AFM). In the case of both isolated aerosol-deposited nanocrystals and those formed by ion implantation and annealing of SiO@sub 2@ films, charging has been accomplished by moving a conducting AFM tip close enough to the nanocrystal to transfer charge. This charging and subsequent discharging were characterized by monitoring the apparent change in nanocrystal height detected by AFM. The trapped charge produces an electrostatic force component that changes the response of the AFM tip, causing a change in the apparent height of the nanocrystal. This mode of electrostatic force microscopy (EFM) together with electrostatic modeling enables quantitative measurement of the trapped charge and discharging dynamics. Simulation enables the EFM sensitivity to be estimated systematically as functions of tip radius and height. Forces due to interaction with this charge and the induced charge on the tip can be determined, and AFM response to these forces can be calculated. Constant-force-gradient contours have been calculated that agree well with measured profiles, and we can determine the amount and location of the injected charge as well as some details of the discharge mechanism. Trapped charge as small 7e is detected in isolated small nanocrystals, and charge in the range 100e - 1000e is observed in larger isolated nanocrystals or embedded nanocrystal ensembles. The combination of EFM imaging and simulations can be used to estimate the homogeneity of the charge density and to probe for high conductance paths within a nanocrystal floating gate. Modeling indicates a discharge mechanism consistent with tunneling through a field-lowered barrier.

4:20pm **EL+NS-TuA8 Quantized Conductance in AuPd Alloy Nanocontacts*, A. Sakai*,** *A. Enomoto, J. Sasaki, S. Kurokawa,* Kyoto University, Japan

Quantization of conductance can be observed most beautifully in Au nanocontacts but much less clearly in transition metals such as Pd. Then, an interesting problem is how the quantized conductance changes by alloying Au with Pd. Do all quantized peaks in the conductance histogram of Au disappear by a small amount of Pd, or do they survive even for Pd-rich nanocontacts? To answer this problem, we have carried out conductance measurements on AuPd nanocontacts in air at room temperature. We prepared Au@sub 1-x@Pd@sub x@ alloy wires with x = 20, 40, 50, 80, and 95 wt%, and measured the transient conductance at the break of two contacting wires. We find that the transition from the conductance behavior of Au to that of Pd takes place gradually with increasing the Pd concentration: sharp peaks in the histogram of Au are suppressed and replaced by a broad and featureless distribution observed in the histogram of Pd. At x = 40 and 50 wt%, both quantized peaks of Au and broad background of Pd coexist in a conductance histogram. This result implies that the conductance of AuPd nanocontacts becomes that of Au or Pd depending on which one of two constituent atoms occupies the narrowest constriction of the contact.

4:40pm **EL+NS-TuA9 Bistability in Conductance of Point Contact formed between a Metal Tip and Ga-terminated Si(111)*, S.L. Pryadkin*,** *D. Chen,* Rowland Institute for Science

Recently, it has been found that voltage-current dependence of a tunnel junction formed by an STM tip and a Ga terminated Si(111) surface exhibits large hysteresis at 77K, similar to that of a double barrier structure.@footnote 1@ This new finding raises the possibility of creating nanoscale storage and switching devices, compatible with silicon technology. To further explore this potential, we have studied the effects of temperature and dopping. It is found that the hystersis exists in a wide range of temperature. Moreover, when the tip is brought to a point contact with the surface, it still gives rise to the bistable transport. This allows us to simplify the junction structure even further and to determine the timing characteristics of this new nanoscale switching/storage device. @FootnoteText@ @footnote 1@ I.B.Altfeder, D.M.Chen Phys.Rev.Lett. 84, p.1284(2000).

5:00pm **EL+NS-TuA10 Analysis of Non-linear Behaviour in Gold Nanowires*, A. Wlasenko*,** *P. Gruetter,* McGill University, Canada

In the presented experiment, a gold nanowire is formed with a mechanical break junction. A voltage bias is applied in the form of a triangle wave (typically 0.1 Hz, 2V@sub pp@) plus a small sine wave (typically 10kHz, 10mV@sub rms@) across the nanowire in series with a load resistor. A current pre-amp measures I(V), while a lock-in amplifier measures its partial derivative with respect to voltage. While others have made I(V) measurements of nanowires (Costa-Kramer et al., PRB 55, 5416 (1997) and Costa-Kramer et al., Nanoscale Science and Technology pp. 1-10 (1998) Kluwer Acedemic), the simultaneous measurement of the derivative allows powerful analysis without choosing a physical model or using mathematical fits. In general, the current is not just a function of voltage [I(X,V)=g(X)f(X,V)]. For instance, the geometry of the nanowire or presence of scatterers should have an effect on the current. The analysis indicates how changes in these non-voltage factors [X] are changing the current [@DELTA@I(@DELTA@X,V)] without having to know explicitly what these are factors are or how they are changing. It is also possible to determine how the form of current f(X,V) is changing with respect to the voltage without knowing g(X). Several individual sets of data shall be investigated that illustrate particular features of both typical and atypical nanowire behaviour. A discussion is presented of the possible physical arguments concerning these features and general trends.

Flat Panel Displays
Room 313 - Session FP+VT-TuA
Emissive Displays and Device Reliability

Moderator: D. Temple, Microelectronics Center of North Carolina

2:00pm **FP+VT-TuA1 Development and Characterization of Cu-Li Alloy Edge Field Emission Devices@footnote 1@*, J.C. Tucek*,** *A.H. Jayatissa, A.R. Krauss, O. Auciello, D.M. Gruen, D.C. Mancini, N. Moldovan,* Argonne National Laboratory

Thin coatings (0.5 - 1 monolayer in thickness) of alkali metals applied to field emission devices are known to significantly enhance field electron emission. However, alkali metals are both physically and chemically unstable in layers exceeding a few Å in thickness, and therefore, it is extremely difficult to fabricate and maintain, during operation, such thin layers on FEAs. Lithium alloy films developed at Argonne National Laboratory provide very stable, low work function coatings that maintain a segregated monolayer of lithium on the surface of the alloy, even under adverse environmental conditions or ion bombardment. These Li-based alloy films have been incorporated into edge emission devices which have low emission thresholds (~3 V/µm), high emission current densities (~10 A/cm@sup 2@), and are physically robust. These devices have been operated in a continuous emission mode for up to 270 hours. After an initial decrease in the emission current level, the emission from the Cu-Li films reach a constant level at approximately 60% of the initial current level, in accord with the stability and the long-lived nature of the Cu-Li films. These devices have been tested in inert gas atmospheres at pressures up to 0.1 mTorr, and they emit (at 50% of the high vacuum level) without catastrophic failure. In addition, we will discuss experiments using a simulated flat panel display configuration and PEEM/FEEM imaging which provide information about the emission uniformity of these edge emitters. Finally, work on applications of the Cu-Li films in gated emission devices will be discussed. @FootnoteText@ @footnote 1@Work supported by the U.S. Department of Energy, BES-Material Sciences, under Contract W-31-109-ENG-38, ONR, and the Office of Naval Research and DARPA under contract N00014-97-F0905.

2:20pm **FP+VT-TuA2 Field Emission Characteristics of Carbon Nanotubes*, B.R. Chalamala*,** *K.A. Dean, R.H. Reuss,* Motorola, Inc. **INVITED**

We will present a summary of our recent work on the field emission characteristics of carbon nanotubes, and discuss their application in functional vacuum microelectronic devices like field emission displays. Our study has two primary goals: gain a deeper understanding of the fundamental mechanisms, and obtain an insight into the impact of practical issues on device performance. In particular, we will present detailed studies on the emission characteristics of individual single walled carbon nanotubes including current saturation mechanisms, device behavior under adverse vacuum conditions, along with high resolution field emission images showing detailed structure.

3:00pm **FP+VT-TuA4 Current Density Saturation in FED Phosphors*, J.S. Lewis*,** University of Florida*; G.O. Mueller, R. Mueller-Mach, T. Trottier,* Agilent Labs*; P.H. Holloway,* University of Florida

In recent years interest in low voltage phosphors has been prompted by the development of field-emission displays (FED's) which operate in the 0.5-6 kV range. Taking into account factors such as dwell time, power density, intrinsic efficiency, and penetration depth, the current densities involved in FED operation are of similar magnitude as those used in CRT's and projection tubes. While brightness typically increases with current, efficiency decreases at higher current densities. Due to the different operating conditions, increased characterization and understanding of saturation at low voltages is needed. Quantification of current density is difficult, since electron beams used to excite the phosphors generally exhibit a Gaussian current distribution. This leads to variation of current density, and potentially saturation effects, over the beam area. Gaussian beam shapes cause more severe saturation in the center of the beam spot where current density is higher, and 'blooming' effects cause a change in beam size or shape as current increases. Deconvolution of these effects is difficult, but new experimental techniques have been developed which for the first time allow the determination of saturation effects in terms of absolute efficiency (under FED conditions). An approach was developed for the determination of the current distribution, and thus the saturation of intrinsic efficiency is obtained as a function of true local current density. The data can be used to model performance under any arbitrary current distribution. Results will be presented for a variety of traditional CRT and projection tube phosphors, as well as newer phosphors for use in FED's. The mechanisms for saturation will be discussed. *This work partially supported by the Phosphor Technology Center of Excellence.

3:20pm **FP+VT-TuA5 Cathodoluminescence from Thin Film versus Powder Phosphors***, **L.C. Williams**, B. Abrams,* University of Florida*; W. Roos,* University of the Orange Free State*; P.H. Holloway,* University of Florida

Thin film cathodoluminescent (CL) phosphors have a number of potential advantages over powder phosphors, such as better mechanical integrity, better thermal heat sinking, more efficient use of material, and better planarity. However most CL screens use powder phosphors due to better brightness, efficiency, and crystallinity. In the current work, we have examined the effects of thin films versus powders on the rate of degradation of ZnS:Mn in residual vacuum gases. The ZnS:Mn thin films were RF planar magnetron sputter deposited onto glass/ITO substrates at a growth temperature of 160°C. The powders were simply cold compacted into shallow stainless steel sample holders. Degradation was shown to occur by the Electron Stimulated Surface Chemical Reaction (ESSCR) mechanism, in which the electron beam dissociated adsorbed oxidizing molecular species (e.g. H@sub 2@O) to cause conversion of luminescent ZnS:Mn to non-luminescent ZnO:Mn. The degradation was faster at low primary beam energy (0.5keV) versus high energy (5keV). Degradation was dependent upon the gas pressure and electron dose (versus time of exposure). Degradation of as deposited thin films was different from that for films annealed at 750°C for 5 minutes; this will be interpreted in terms of the point defect density of as deposited versus annealed phosphor films. After correction for the true surface area of powders versus films, the rate of degradation will be compared. The mechanisms leading to the different degradation rates for films versus powders will be discussed.

3:40pm **FP+VT-TuA6 Reliability of Silicon-based Field Emission Displays***, **T. Akinwande**,* Massachusetts Institutute of Technology **INVITED**

PLEASE SEND US AN ABSTRACT. Thank you.

4:20pm **FP+VT-TuA8 Illumination Sources for Laser-based Displays***, **B. Bischel**,* Gemfire Corporation **INVITED**

PLEASE SEND US AN ABSTRACT. Thank you.

5:00pm **FP+VT-TuA10 Oxide Phosphor TFEL Devices Fabricated by Magnetron Sputtering with RTA***, **T. Minami**, H. Toda, T. Miyata,* Kanazawa Institute of Technology, Japan

High luminance thin-film electroluminescent (TFEL) devices using various oxide phosphor thin films have been recently reported. However, a high luminance could only be obtained in these TFEL devices by postannealing in various atmospheres at high temperatures about 1000@super o@C. In this paper, we describe a procedure for producing high luminance TFEL devices with an oxide phosphor thin-film emitting layer prepared without high temperature postannealing: magnetron sputtering with rapid thermal annealing (RTA). TFEL devices were fabricated by depositing oxide phosphor thin films onto thick sintered BaTiO@sub 3@ insulating ceramic sheets. A Ga@sub 2@O@sub 3@:Mn or ZnGa@sub 2@O@sub 4@:Mn thin film was deposited by r.f. magnetron sputtering onto a substrate mounted on a rotating platform; a thin film was deposited onto the substrate when it passed over the target, and subsequently, RTA was performed on the deposited film when it passed over the halogen lamps. The sputter deposition under a platform rotation of 1-2 r.p.m. was carried out in an Ar+O@sub 2@ sputter gas atmosphere at pressures of 0.2-8 Pa with an rf power of 120 W. High luminance green emissions were obtained in TFEL devices using either a Ga@sub 2@O@sub 3@:Mn or a ZnGa@sub 2@O@sub 4@:Mn thin-film emitting layer prepared without postannealing at high temperatures under optimized deposition conditions. The Ga@sub 2@O@sub 3@:Mn and ZnGa@sub 2@O@sub 4@:Mn TFEL devices driven by a sinusoidal wave voltage at 1 kHz exhibited luminances of 24 and 200 cd/m@super 2@, respectively.

Incorporating Principles of Industrial Ecology
Room 304 - Session IE-TuA

Green Manufacturing

Moderator: P.M. Beauchamp, Jet Propulsion Laboratory

2:00pm **IE-TuA1 Challenges in Bringing Green Manufacturing Technologies to the Clean Room Floor***, **S. Raoux**,* Applied Materials **INVITED**

The semiconductor industry is undertaking major research and development efforts to reduce the environmental impact of its manufacturing processes. In particular, technologies have been introduced to eliminate atmospheric emissions of global warming compounds, reduce solid waste and conserve energy and water resources. At each technology node, semiconductor fabrication processes are amenable to change, and implementation of sustainable manufacturing practices should be favored. However, the stringent requirements of the semiconductor fabrication process render the introduction of novel manufacturing techniques a challenge. In this talk, we present innovative concepts that have been developed and integrated within semiconductor fabrication tools. Emphasis is placed on point-of-use (POU) solutions and environmental engineering using plasma technologies. We review the requirements that must be met by green technologies to be integrated to a complex manufacturing environment. We also present arguments to demonstrate that environmentally benign manufacturing methods can be developed and implemented in an economically viable way.

2:40pm **IE-TuA3 Eliminating Perfluorocompound Gas Emissions from CVD Chamber Cleans***, **P.J. Maroulis**, A.D. Johnson, W.R. Entley,* Air Products and Chemicals, Inc. **INVITED**

Perfluorocompond (PFC) gases such as CF4, C2F6, and NF3 are used extensively in semiconductor manufacturing processes. The largest volume use for these gases is for chamber cleaning following chemical vapor deposition (CVD). PFCs have long atmospheric lifetimes and absorb strongly in the infrared region of the electromagnetic spectrum where the earth's atmosphere would otherwise be transparent. Because of their infrared absorbances and persistence, PFCs are suspected of contributing to global warming. Through the World Semiconductor Council (WSC) the global semiconductor industry has voluntarily committed to reduce its cumulative emissions of perfluorocompounds. For the U.S., Europe, and Japan, PFC emissions will be reduced to 90% of 1995 levels by 2010 with some companies announcing even more aggressive reduction targets. Based on industry growth projections, substantial reductions for individual processes will be necessary to achieve these targeted levels. Both process optimization of traditional C2F6 based in situ cleans and substitution of NF3 for C2F6 in situ cleans are effective strategies for reducing the environmental impact of installed CVD tools. For new CVD tools, the manufacturers of semiconductor process equipment have developed and introduced a new remote NF3 cleaning technology that essentially eliminates PFC emissions. The combination of these three strategies, optimization of traditional C2F6 based in situ cleans, the substitution of NF3 for C2F6 in in situ cleans, and the implementation of the remote clean technology, has effectively solved the semiconductor industry's PFC issue. This presentation will contain data demonstrating the effectiveness of these strategies. In essentially all cases, perfluorocompounds emissions have been reduced by 50% to >99%.

3:20pm **IE-TuA5 Meeting IBM's PFC Emission Goals: Using the IBM In Situ Dilute NF@sub 3@/He Plasma Clean in Production on the Applied Materials 200 mm P5000 Lamp-Heated CVD Toolset***, **C.M. Hines**,* IBM Microelectronics*; W.R. Entley, R.V. Pearce, A.D. Johnson,* Air Products and Chemicals, Inc.

The major use of perfluorocompounds (PFCs) in semiconductor manufacturing is for residue removal following thin film deposition in chemical vapor deposition (CVD) chambers. One promising strategy to reduce PFC emissions in CVD chambers is the use of alternative clean gases that have lower global warming potentials and inherently higher utilization efficiencies (the percentage of the PFC that is consumed during the clean process) than the traditionally used carbon based PFCs, CF@sub 4@ and C@sub 2@F@sub 6@. Using this strategy, IBM developed a one-step in situ dilute nitrogen trifluoride/helium (NF@sub 3@/He) clean to replace the process of record (POR) C@sub 2@F@sub 6@-based cleans used in their Applied Materials (AMAT) 200mm Precision 5000 lamp-heated (DxL)

CVD chambers. Successful implementation of the dilute NF@sub 3@/He clean into production is considered key to IBM meeting its PFC reduction goals. Using quadrupole mass spectrometry (QMS) and Fourier transform infrared (FTIR) spectroscopy the process emissions of IBM's POR C@sub 2@F@sub 6@-based cleans and the new one-step dilute NF@sub 3@/He clean following deposition of both phosphosilicate glass (PSG) and tetraethylorthosilicate (TEOS) oxide were quantified. For TEOS oxide deposition the one-step dilute NF@sub 3@/He clean reduced the MMTCE value of the clean by 99 % with respect to the POR C@sub 2@F@sub 6@ clean. For PSG deposition, the one-step dilute NF@sub 3@/He clean reduced the MMTCE value of the POR clean by 96 %. In addition, the one-step dilute NF@sub 3@/He clean significantly reduced the total combined volumetric emissions of F@sub 2@ and HF compared to the POR C@sub 2@F@sub 6@ cleans. This presentation will include an overview of the implementation of the NF@sub 3@/He clean, current production data including tool performance (particles, mean time between wetstrips, etc.), and clean time/emissions comparisons between the POR C@sub 2@F@sub 6@ cleans and the one-step NF@sub 3@/He clean.

3:40pm **IE-TuA6 Treatment of Wastes from Chemical Mechanical Polishing Operations***, **S. Raghavan**, Y. Sun, J. Baygents,* University of Arizona **INVITED**

Chemical mechanical planarization (CMP) of dielectrics and metals has emerged as one of the most important techniques used in the fabrication of integrated circuits. In this technique, dielectric and metal films are globally and locally planarized using particulate slurries made from submicron-sized alumina and silica particles. A multi platen CMP tool can typically process 40 wafers per hour at a slurry consumption of approximately 100 ml/min/wafer. The aforementioned tool, if integrated with a cleaner, will require two to three gallons per minute of DI water. The mixing of CMP waste with the post-CMP cleaning waste typically results in a waste stream that is a very dilute dispersion of solids containing approximately 500 to 5000 ppm solids. In the case of metal CMP, the waste is likely to contain metal ions, unreacted oxidant such as hydrogen peroxide, residual corrosion inhibitors and other additives that are present in the slurry. Wastes from copper CMP may contain anywhere between 10 and 40 ppm of dissolved copper, in the uncomplexed and complexed form. By the year 2002, chemical mechanical planarization processes are expected to account for thirty percent of water consumed in a fabrication facility. Because of this statistics, increasing pressure is put upon fabrication facilities to treat the CMP wastes and recycle the water. Additionally, environmental regulations at the local and national level demand that solids and copper ions be removed before disposal of the water to publicly owned treatment facilities. In this presentation, an overview of the CMP waste problem will be provided and various techniques available for the treatment of CMP wastes will be critically reviewed.

4:20pm **IE-TuA8 Advanced Chemicals for Semiconductor Processing***, **E.R. Sparks**, W. Wojtczak, S.A. Fine,* ATMI **INVITED**

Three of the challenges to semiconductor processing are shrinking dimensions, copper metallization, and low-k dielectric materials. These challenges have been successfully addressed with a new group of water-based chemicals that fortuitously have very favorable properties. - As lithographic dimensions shrink, etching and other processing parameters become more stringent. The residues created from photoresist during these proceses often incorporate fluorocarbon residues, and silicon and metal oxides that are impossible to remove with traditional chemicals. - New processes using copper damascene metallization have additional constraints, as many traditional chemicals are not benign to copper. - Higher speed devices are attainable with low-k dielectric materials, but these materials have special chemical requirements. Advances have been made to meet all three of these requirements by formulating chemical mixtures that are more benign, both environmentally and regarding health issues, than previously possible. These blends are water-based, water-rinsable, and free of regulated solvents, i.e., "green". The resulting technology has a very favorable cost of ownership due to lower costs related to abatement and disposal, compared to more traditional solvent blends.

5:00pm **IE-TuA10 High Throughput Process for Photoresist Stripping and Residual Polymer Removal in a Via Post-Etch Process***, **M. Boumerzoug**, Q. Geng, H. Xu,* Ulvac Technologies Inc.*; S. Gu,* LSI Logic Corporation*; S. Goh,* Silterra (M) Sdn. Bhd.*; T. Meyer, J. Seaton,* LSI Logic Corporation

In fabricating advanced IC, a multi-level interconnect scheme is commonly used and plasma etch is applied to form metal lines and via holes. During the plasma etch, a sidewall polymer is formed to control the etch profile. After the etch, the sidewall polymer needs to be removed completely to insure a good via contact resistance. Typically, a very aggressive amine based chemical solvent is needed to clean up the sidewall polymer. As the design rule shrinks and aggressive zero overplot of the metal line and via plug is used to minimize the die size, some degree of misalignment between via plug and metal lines is inevitable. Wet chemical based post etch cleaning starts to show problems for the misaligned via and metal because they may attack exposed Ti, W and Al. An advanced dry clean process has been developed for removing post etch polymer. In addition, the dry clean process offers a lower cost of ownership (COO) than the wet clean process and is much safer and environmentally friendly. This technology utilizes the combination of microwave downstream and non-damage ion assisted processes to strip chemically altered and damaged photoresist and clean residue according to the chemical composition of each layer. The ion-assisted process is also found useful in stripping the photoresist at high rate. After this dry process, no wet strippers are needed; thus, the high cost and environment and safety concern associated with chemicals can be eliminated. In some cases, this dry clean process becomes an enabling technology for avoiding Ti and W-plug attack occurring in the wet cleaning processes. Split lots of wafers, which have two layer metal, were processed by the all-dry processes and tested electrically. The via chain resistance, metal bridging yield, metal continuity and electrical CD are all equal or better than the control wafers which were processed by wet chemicals.

Material Characterization
Room 207 - Session MC-TuA

Quantitative Surface Analysis

Moderator: S. Hofmann, Max-Planck-Institute for Metals Research

2:00pm **MC-TuA1 Molecular Secondary Particle Emission from UHV-Prepared Molecular Overlayers***, **A. Schnieders**, M. Schröder, K. Rüschenschmidt, A. Benninghoven, H.F. Arlinghaus,* Physikalisches Institut der Universität Münster, Germany

Secondary particle yields in organic SIMS and SNMS are not determined by the surface concentration of the respective particles only. Furthermore, the chemical interaction between substrate and adsorbed molecules determines the secondary particle emission, in particular from the first molecular monolayer. Especially the intrinsic ionization but also the fragmentation of the sputtered particles is influenced by this so-called matrix effect. Additionally, secondary particle emission depends on primary ion properties such as species or energy. In continuation of recent investigations, mainly focussing on the sputter process, we used UHV-prepared molecular overlayers of adenine and alanine prepared on liquid-nitrogen cooled substrates. We extended our investigations to a broader range of substrate/molecule combinations to determine the influence of the matrix effect. The flux of sputtered secondary neutrals and secondary ions in dependence on the layer thickness was continuously monitored under static sputtering conditions during overlayer formation. The detection of the sputtered neutrals was achieved by efficient laser postionization. As substrates we chose Au, Ag, Cu, Ni, Si, Al and C surfaces to cover different types of surface chemistry. A comparison between secondary ion and secondary neutral emissions showed a distinct ionization matrix effect depending on the respective substrate material for @beta@-alanine but not for adenine.

2:20pm **MC-TuA2 Detection of Trace Metal Contamination on Si Wafers by TOF-SIMS***, **R. Möllers**, T. Grehl, E. Niehuis,* ION-TOF GmbH, Germany

According to the ITRS roadmap, the detection of metal trace impurities on wafer surfaces is becoming increasingly important. Analytical techniques with detection limits for transition metals and alkali metals well below 5E8 atoms/cm@super 2@ are required in the coming years. At present, TXRF is widely used for the detection of transition metals on blank wafers but it seems that its detection limits will no longer be sufficient in the future. The VPD based methods collect the contamination from the oxide of the entire wafer and techniques like VPD-AAS and VPD-ICMS can achieve detection limits in the low E8 range. However, they can not give information on the lateral distribution and do not discriminate against particle contamination. Time-of-Flight SIMS is an attractive candidate for the detection of trace metals. The analysed area is only about 50 to 100 µm in size and the analysis for all elements in parallel takes only a few minutes per position on a wafer. Detection limits in the low E8 range can be achieved for a number of important metals. In combination with a stage raster, mapping of contaminants on large areas is possible. In contrast to the established techniques, TOF-SIMS can be applied to patterned wafers and the wafer back-side as well. On the other hand, the quantification in TOF-SIMS surface analysis has been a concern due to the well known matrix effect of SIMS and the rather small sampling depth of only 1-2 monolayers. In this contribution, we will discuss the capabilities of TOF-SIMS for trace metal analysis in more detail. We will focus on analytical protocols that give quantitative results and minimise the influence of the initial chemical state of the surface (organic contamination level, oxidation state etc.). The results will be compared to the established analytical techniques.

2:40pm **MC-TuA3 Comparative Ion Yields by Secondary Ion Mass Spectrometry from Microelectronic Films***, **C. Parks,*** IBM Corporation

Secondary Ion Mass Spectrometry (SIMS) is reported from multiple-element ion implants. The implants include a thirteen element metal set dubbed the Universal Metal Standard (UMS) and a six element gas set called the Universal Gas Standard (UGS). These implants were made into films of interest for microelectronics (silicon, silicides, wiring layers, liner metals, organic dielectrics, and polymer dielectrics.) Because species are co-implanted, the relative sensitivity factor (RSF) for many elements are generated with each SIMS profile. Because the implant sets are self-consistent, ion yields can be readily compared from matrix to matrix. The literature has compared ion yields within single matrices using the RSF. This study performs a broader comparison across matrices and requires a more general metric. In SIMS, the useful ion yields of potassium positive ions and chlorine negative ions approach a yield-saturating limit. To compare matrices, we obtain normalized useful yields (NUY), where the normalization is to the potassium or chlorine yields from silicon. In this paper we document the ion implants sets themselves, we show some of the SIMS profiles, and we note trends in ion yields and implications for SIMS analysis.

3:00pm **MC-TuA4 Quantitative Surface Analysis Using Ion Implantation***,* ***F.A. Stevie****, J.M. McKinley, C.N. Granger,* Lucent Technologies*; F. Hillion,* CAMECA Instruments*; D.S. Simons, P. Chi,* National Institute of Standards and Technology*; B. Schueler,* Physical Electronics*; C.B. Vartuli, T.L. Shofner,* Lucent Technologies*; L.A. Giannuzzi,* University of Central Florida **INVITED**

This paper summarizes current uses of ion implantation to quantify analytical data. SIMS is emphasized, but the methods are applicable to other techniques. SIMS requires secondary standards for calibration. Ion implantation has been traditionally used to create SIMS standards because any element can be implanted and the dose and energy tailored for the application. High reproducibility has been demonstated for SIMS measurements using these standards. Absolute dose measurements can be made for boron and arsenic using NIST reference materials. Quantification at a surface can be achieved using implantation through a removable layer by selecting the implant energy so that the peak of the implant is at the interface between the removable layer and the substrate. This mehod has been successful for surface SIMS, time-of-flight SIMS, and TXRF measurements. The dose can be increased to provide detection and quantification by other analytical methods, such as AES, XPS, and EDS. High dose quantification can also be used to quantify SIMS in the concentation range of a few percent. This is especially of interest for semiconductor materials, such as PSG, BPSG, and FSG, that are difficult to profile by other methods. SIMS line scan measurements can be quantified by first scanning over a series of depth profiles made at increasing depth into an ion implanted reference. Focused ion beam (FIB) workstations can be used to prepare cross sections of ion implanted standards that can be lifted out and mounted perpendicular to the analysis beam. Secondary ion images of the cross sections provide quantification of the element of interest. FIB prepared cross sections of high dose implanted standards can be used for AES and EDS calibration asnd for determination of detection limit.

3:40pm **MC-TuA6 Comparison of ISS, XPS, and QUASES-XPS Techniques for Determination of Growth Mechanisms: Application to Thin Iron Oxide Films Deposited on SiO2***,* ***F. Yubero****, A.R. Gonzalez-Elipe,* Inst. for Material Science of Sevilla*; S. Tougaard,* University of Southern Denmark, Denmark

We have studied the formation of iron oxides on SiO2 under varying growth conditions by X-ray photoemission spectroscopy (XPS) and ion scattering spectroscopy (ISS). Three different procedures for quantitative analysis of the experimental data were used: 1) traditional analysis of the XPS-peak intensity by assuming a layer formation that covers the surface completely, 2) combination of the XPS-peak and ISS intensities assuming a Poisson distribution of island heights, and 3) Tougaard-method (QUASES@footnote 1@) to determine in-depth profiles from analysis of the peak and background. The difference between the three methods lies mainly in the a priori assumptions made on the surface morphology. In contrast to method 1) and 2), the Tougaard-method is free from assumptions about the growth structure of the overlayer. By a critical comparison of the results, it is concluded that the Tougaard-method gives the most complete and reliable information. It is found that iron oxides on SiO2 grow with strong island formation, whose height depends on the preparation conditions of the deposit. The growth mechanisms are proposed. Thus, for example, if iron oxide is deposited on SiO2 at room temperature in a PO2 of 2Â´10-6 mbar, islands of ~22@Ao@ homogeneous thickness are formed for surface coverages below 20%. If the samples are annealed at 773K in a PO2 ~4Â´10-5, higher islands are formed (~32 @Ao@). For iron oxide treated by a plasma of oxygen, ~40 @Ao@ tall islands are formed for surface coverages below 30%. Besides, even ~35 @Ao@ of iron oxide does not fully cover the SiO2 substrate surface. Strong shadowing effects are observed in the ISS signal from the iron oxide deposits on SiO2 due to the tall island formation. As expected, the shadowing effects are stronger when taller islands have been formed. @FootnoteText@ @footnote 1@ http://www.quases.com

4:00pm **MC-TuA7 Quantitative Depth Profiling with Angle Resolved XPS: The Effect of Surface Roughness***,* ***S.M. Hunt,*** Montana State University*; B.J. Tyler,* University of Utah

A major limitation of conventional XPS is that sample concentrations are calculated based on the assumption that the elemental concentrations are homogeneous in the outer 100 angstroms, an assumption that is frequently inaccurate. By exploiting the angular dependence of the XPS sampling depth, it is easy to get a qualitative assessment of surface uniformity, however, quantitative use of the data can be problematic. The objective of this work has been to explore the limits to which ARXPS data can be used for quantitative analysis of depth profiles and in particular to explore the influence of surface roughness on quantitation. Because calculating concentration depth profiles for ARXPS data is a mathematically unstable problem, modeling studies are necessary to determine how various sources of error propagate through the calculations. Assessing the influence of different types of error is of importance because even relatively small errors in the data might propagate into large errors in the calculated profiles. The influences of random error and surface roughness have been investigated. Monte Carlo simulations were used to explore the effects of random error. To explore the influence of roughness, simulations were used to calculate the XPS signal intensities from surfaces described by a 2 dimensional wave function. Various amplitude to wavelength ratios were explored. The influence on both the measure signal intensities and the calculated depth profiles has been investigated. The results have been validated on a series of samples consisting of self-assembled monolayers. Except at glancing angles, surface roughness has a minimal effect. At angles greater than 70 degrees from the surface normal, even minimal surface roughness can result in changes in the measured signal intensity of greater than 1000%. Optimum parameters for ARXPS experiments and the calculations have been identified.

4:20pm **MC-TuA8 Intercomparison of IMFPs Determined by Elastic Peak Electron Spectroscopy***,* ***S. Tougaard,*** University of Southern Denmark, Denmark*; M. Krawczyk, A. Jablonski,* Polish Academy of Sciences*; J. Pavluch,* Dept. Electronics and Vacuum Physics, Czech Rep.*; J. Toth, D. Varga, G. Gergerly, M. Menyhard, A. Sulyok,* Hungarian Academy of Sciences

We have evaluated the consistency and accuracy of IMFPs determined from comparison of the intensity of elastically reflected electrons with theoretical calculations. The scatter in determined IMFPs with experimental geometry, spectrometer energy resolution and the procedure for background subtraction was determined. Four spectrometers with widely different geometries and energy resolutions, placed in four different laboratories in three countries were used. Four background subtraction methods (Shirley, linear, Tougaard, and ELPSEP) were applied to isolate the elastic peak intensity from the reflected electron spectra. The RMS deviation of the IMFP from a function fitted to the data is 3.01 - 4.11 A depending on the background subtraction method and it is smallest for the Tougaard method. The RMS deviation from IMFP values calculated by Tanuma et al is 3.41 - 4.41 A again with the smallest value for the Tougaard method. The mean percentage deviation from the Tanuma et al values is ~ 18 %. The results point to the conclusion that the major contribution to the inaccuracies in IMFPs determined with the elastic peak method is not the background subtraction procedure but rather lack of accuracy of the presently available models for elastic electron scattering, i.e. atomic elastic scattering cross sections and effects of crystallinity that are not included in the presently applied models. @FootnoteText@ @footnote@ Work supported by EU contract INCO COPERNICUS ERBIC15CT960800.

4:40pm **MC-TuA9 Measurement of Silicon Dioxide Film Thicknesses by XPS*, C.J. Powell,*** National Institute of Standards and Technology*; A. Jablonski,* Polish Academy of Sciences

It is now customary for the effects of elastic-electron scattering to be ignored in measurements of overlayer thicknesses by XPS. It is known, however, that elastic scattering can cause the effective attenuation length (EAL), needed for the thickness measurement,@footnote 1@ to be appreciably different from the corresponding inelastic mean free path.@footnote 2@ We have investigated the effects of elastic-electron scattering in measurements of the thicknesses of SiO@sub 2@ films on Si from XPS measurements with Al and Mg K@alpha@ x rays. Calculations have been made of substrate and oxide Si 2p photoelectron currents for different oxide thicknesses and emission angles using an algorithm based on the transport approximation.@footnote 3@ This algorithm accounts for the occurrence of elastic scattering along electron trajectories in the solid. It was found that the average EAL, determined from the substrate currents with and without an oxide overlayer of a certain thickness, varied weakly with oxide thickness and emission angle for a restricted range of emission angles. For emission angles greater than about 60°, corrections need to be made to this average EAL in order to determine the oxide thickness. These corrections will be described.@FootnoteText@ @footnote 1@A. Jablonski and C. J. Powell, Surf. Interface Anal. 20, 771 (1993). @footnote 2@A. Jablonski and C. J. Powell, J. Electron Spectrosc. 100, 137 (1999). @footnote 3@I. S. Tilinin, J. Zemek, and S. Hucek, Surf. Interface Anal. 25, 683 (1997).

5:00pm **MC-TuA10 A New Angle on Angle Dependent XPS*, K.S. Robinson,*** *G. Jones, R. White, J. Wolstenholme,* VG Scientific, UK

Angle dependent XPS offers the ability to determine relative distributions, compositions and layer thickness for layers thinner than the XPS analysis depth. In practice, the use of angle dependent XPS is limited by the need to acquire data at several angles, usually requiring the sample to be tilted. The analysis of small features is also difficult because tilting the sample changes the analysis area as the projected shapes of the X-ray spot and / or analysis area on the sample change. We previously presented results@footnote 1@ from a commercial instrument where the electron input lens could be used to sequentially define two angles; a surface sensitive angle and a bulk sensitive angle, allowing angle dependent XPS without moving the sample. This method has now been extended to allow simultaneous collection of angle dependent XPS data from a range of angles. We present data from this instrument which shows the application to oxide thickness measurements and more complex structures. @FootnoteText@@footnote 1@QSA-10 at University of Surrey, UK, 1998.

Magnetic Interfaces and Nanostructures
Room 206 - Session MI+NS+NANO 6-TuA

Magnetic Imaging II

Moderator: F.J. Himpsel, University of Wisconsin, Madison

2:00pm **MI+NS+NANO 6-TuA1 Correlation of Ferromagnetic and Antiferromagnetic Spin Orientation Observed by Photoemission Electron Microscopy*, S. Anders,*** *A. Scholl, F. Nolting, H.A. Padmore,* Lawrence Berkeley National Laboratory*; J. Stohr, J. Luening,* Stanford Synchrotron Radiation Laboratory*; J.W. Seo,* University of Neuchatel, Switzerland*; J. Fompeyrine, J.-P. Locquet,* IBM Research Division, Switzerland*; M. Scheinfein,* FEI Company **INVITED**

Photoelectron emission microscopy (PEEM) using polarized x rays is a unique tool for the study of ferromagnetic (FM) and antiferromagnetic (AFM) materials. FM materials are studied using x-ray magnetic circular dichroism (XMCD) and AFM materials using x-ray magnetic linear dichroism (XMLD). The elemental specificity of PEEM allows to study individual layers in multilayer structures, and to investigate the coupling between them. Increasingly complex layered structures containing magnetic and antiferromagnetic materials are used in modern magnetic devices, and knowledge of the magnetic properties of the layers and interfaces is essential for the understanding of the properties of these devices. Of particular interest is the effect of exchange biasing at the interface of an AFM and an FM. AFM materials have been difficult to study so far because of a lack of methods with sufficient spatial resolution and surface sensitivity. We have investigated the magnetic and topographic surface structure of several AFM materials, in particular thin singlecrystalline and polycrystalline NiO and LaFeO@sub 3@ films. We were able to resolve the antiferromagnetic surface structure of those materials, showing antiferromagnetic domains, and antiferromagnetic patterns, correlated to the surface topography. Local NEXAFS spectra yielded information about the antiferromagnetic orientation at the sample surface. The study of an FM Co thin film on top of an AFM LaFeO@sub 3@ film showed for the first time a direct correlation between AFM and FM domains.

2:40pm **MI+NS+NANO 6-TuA3 Magnetic Imaging of NiO/Ag(001) Thin Film using PhotoEmission Electron Microscope*, W. Zhu,*** University of Connecticut, US*; L. Seve, B. Sinkovic,* University of Connecticut*; A. Scholl, S. Anders,* Lawrence Berkeley National Laboratory

PhontoEmission Electron Microscope (PEEM) combined with linearly polarized synchrotron X-rays provides a powerful way of imaging magnetic domains in antiferromagentic thin films. We have performed magnetic imaging on antiferromagnetic thin film of NiO with PEEM. The 90-Å thick NiO film is of (001) orientation, epitaxially grown on a Ag (001) single crystal substrate. The magnetic contrast is found to be correlated with the topological contrast, which is caused by the local thickness variation in the film. Micro-X-ray absorption spectra (XAS) in areas of different contrast revealed that the directions of magnetic moments within these areas are differently oriented with respect to the X-ray polarization direction. The difference in Micro-XAS from these areas disappeared at temperature of ~350 °C (above the Neel temperature), where the antiferromagnetic order disappears. Experiments with the X-ray polarization direction parallel to [100] and [110] direction of the film give similar results, which indicates that the magnetic contrast is due to the in-plane vs. out-of-plane magnetic moments orientation rather than the differently oriented in-plane moments. These results are consistent with our recent spectroscopic studies of NiO/Ag(001) films of various thickness.

3:00pm **MI+NS+NANO 6-TuA4 Magnetic Imaging by Local Tunneling Magnetoresistance - A High Resolution Technique*, W. Wulfhekel,*** *H.F. Ding, J. Kirschner,* MPI Halle, Germany **INVITED**

We give an overview over our recent efforts of magnetic imaging using scanning tunneling microscopy with a ferromagnetic tip. Magnetic sensitivity is obtained on the basis of local tunneling magnetoresistance between a soft magnetic tip and the sample. The imaging capacities of the technique are illustrated with exemplary studies of the surface domain structure of different itinerant ferromagnets. On Co(0001) we find surprisingly narrow sections of the walls of only 1.1nm width, over an order of magnitude less than previously observed in Co. Recording quantitative profiles of the perpendicular component of the magnetization across the wall and comparing the experimental data with micromagnetic calculation, the narrow sections are identified as 20° domain walls. Besides magnetic imaging, we focus on the influence of the stray filed of the tip on the magnetic structures under investigation. In the limit of soft magnetic materials or strong stray fields, the wall mobility and magnetic susceptibility can be studied on the local scale. Finally, measurements of magnetoresistance versus tunneling voltage and tip sample distance give deeper insight into the mechanisms of spin polarized tunneling.

3:40pm **MI+NS+NANO 6-TuA6 Self-assembled Magnetic Nanowires Studied with Spin-polarized Scanning Tunneling Microscopy*, T.-H. Kim,*** *W.-G. Park, Y. Obukhov, Y. Kuk,* Seoul National University, Korea

In thin film of immiscible Co and Ag alloys, nanowires have been observed. The alternating stripes, magnetic Co stripes and non-magnetic Ag stripes, are formed on W(110) substrate by the driving force of the phase separation. The film can be grown sequentially, or deposited simultaneously. The periods of the stripes are found to be 20 to 30 Å, perpendicular to the long axis of the stripes. The relations between the morphology and the magnetic contrast of the self-assembled magnetic nanowires have been studied with spin-polarized scanning tunneling microscopy. Using an electromagnet for tip magnetization, the magnetic field can be applied to the soft magnetic tip both parallel and perpendicular to the axis of the tip. With this setup, we are able to image the direction of the magnetization of the sample.

4:00pm **MI+NS+NANO 6-TuA7 Direct Visualization of Magnetic Nanowires by Spin-Polarized Scanning Tunneling Spectroscopy*, O. Pietzsch,*** *A. Kubetzka, M. Bode, R. Wiesendanger,* University of Hamburg, Germany

While scanning tunneling microscopy (STM) and spectroscopy (STS) are the established methods of choice for the study of structural and electronic surface properties at ultimate real space resolution, no equivalent technique for magnetic imaging was available so far. The most widely applied surface sensitive methods as, e. g., magneto-optical Kerr effect

(MOKE), average over comparably large sample fractions. Here we present a recent spin-polarized STS study, carried out with an STM especially designed for magnetic imaging.@footnote 1@ We will show high resolution images of a self-organized array of Fe nanowires grown on a stepped W(110) single crystal.@footnote 2@ The magnetic wires have a periodicity of 8 nm, an average width of 4 nm, and a thickness of two atomic layers. Making use of ferromagnetically coated STM tips with the appropriate anisotropy we were able to image the magnetic domain structure in detail. The magnetism of the stripe system is governed by perpendicular anisotropy.@footnote 3@ Adjacent stripes exhibit antiferromagnetic coupling mediated by the stray field. Our images allow the investigation of the influence of local structural defects as, e. g., non-uniform stripe width or dislocation lines, on the magnetic properties on a sub-nanometer scale. The width and orientation of domain walls within single stripes is determined. We will show how the domain structure is affected by applied external fields of up to 0.5 Tesla. The contrast mechanism will be explained. The imaging method is of general applicability for the study of the surfaces of magnetic nanostructures. @FootnoteText@ @footnote 1@ O. Pietzsch et al., Rev. Sci. Instrum. 71, 424 (2000) @footnote 2@ O. Pietzsch, A. Kubetzka, M. Bode, and R. Wiesendanger, Phys. Rev. Lett. , in press. @footnote 3@ J. Hauschild, U. Gradmann, and H. J. Elmers, Appl. Phys. Lett. 72, 3211 (1998).

4:20pm **MI+NS+NANO 6-TuA8 Real-Space Imaging of Two-Dimensional Antiferromagnetism on the Atomic Scale*, M. Bode,*** University of Hamburg, Germany*; S. Heinze,* Forschungszentrum Jülich, Germany*; A. Kubetzka, O. Pietzsch,* University of Hamburg, Germany*; X. Nie, S. Blügel,* Forschungszentrum Jülich, Germany*; R. Wiesendanger,* University of Hamburg, Germany

The ultimate limit of two-dimensional antiferromagnetism (2D-AFM) is a magnetic monolayer of chemically equivalent atoms, where adjacent atoms at nearest-neighbor sites have magnetic moments with opposite directions, deposited on a non-magnetic substrate.@footnote 1@ Since the total magnetization of this film is zero spatially averaging techniques like spin-polarized photoelectron spectroscopy cannot be used for an experimental verification of (2D-AFM). We have resolved the two-dimensional antiferromagnetic structure within a pseudomorphic monolayer film of chemically identical manganese atoms on tungsten (110) by spin-polarized scanning tunneling microscopy (SP-STM) at 16 Kelvin.@footnote 2@ While images of the chemical surface unit-cell without any magnetic contribution were obtained using a non-magnetic W-tip, spin-polarized electrons from magnetically coated tips probe the change in translational symmetry due to the magnetic c(2x2)-superstructure of Mn/W(110). Based on fundamental theoretical arguments it will be shown that SP-STM is a powerful technique for the investigation of complicated surface magnetic configurations. @FootnoteText@ @footnote 1@ S. Blügel, M. Weinert, and P.H. Dederichs, Phys. Rev. Lett. 60, 1077 (1988). @footnote 2@ O. Pietzsch et al., Rev. Sci. Instr. 71, 424 (2000).

4:40pm **MI+NS+NANO 6-TuA9 Ballistic Electron Magnetic Microscopy Studies of Ferromagnetic Films and Tunnel Junctions*, W.H. Rippard,*** *A.C. Perrella, R.A. Buhrman,* Cornell University **INVITED**

A new magnetic imaging technique, ballistic electron magnetic microscopy (BEMM), has been developed to study the magnetic structure in ferromagnetic multilayer films and nanostructures as a function of magnetic field H. In BEMM we exploit the hot electron transport properties of the ferromagnetic films in order to probe their magnetic structure. This technique allows not only the magnetic imaging in applied fields with nm-scale spatial resolution, but also allows the direct investigation of spin dependent transport through the ferromagnetic multilayers. As we are not using a magnetic probe to image these films, we are able to investigate very thin and soft magnetic structures which are the most relevant to technological applications. The magnetization reversal process of both continuous and patterned ferromagnetic films have been investigated. Using a UHV compatible stencil-mask technique, sub-micron structures have been fabricated and imaged with BEMM. In particular, I will discuss the switching behavior of permalloy 'diamonds' and 'rectangles' (1.5 x 0.3 microns2), as well as other shapes of smaller dimension. Using this technique the nanometer scale imaging of tunnel junctions can also be performed. Ballistic current transport through magnetic tunnel junctions will be presented, both in terms of the imaging of 'pin holes' in the junctions and spin-dependent transport through the barrier. The energy dependence of the transport in the ferromagnetic multilayer structures as well as in the tunnel junction systems will also be presented.

Processing at the Nanoscale/NANO 6
Room 302 - Session NS+NANO6+SS+MC-TuA

Self-assembly and Self-organization

Moderator: R. Wiesendanger, University of Hamburg, Germany

2:00pm **NS+NANO6+SS+MC-TuA1 Dip-Pen Nanolithography: A New Tool for Generating and Studying Soft Nanostructures*, C.A. Mirkin,*** *S.A. Brennan, L.M. Demers, S. Hong, P.V. Schwartz, D.A. Weinberger,* Northwestern University **INVITED**

A new type of ultrahigh resolution soft-lithography, Dip-Pen Nanolithography (DPN) that is interfaceable with biomolecules and biofunctionalized building blocks will be presented. This soft lithography allows one to routinely pattern structures, in serial or parallel fashion, with sub 50 nm spatial and line-width resolution with near-perfect alignment. Implications in materials synthesis, electronics, and biodiagnostics will be discussed.

2:40pm **NS+NANO6+SS+MC-TuA3 A Step Toward Making and Wiring-up Molecular-Scale Devices with a Self-Directed Growth Process***, G.P. Lopinski, D.D.M. Wayner, D.J. Moffatt,* National Research Council of Canada*; **R.A. Wolkow,*** National Research Council of Canada, Canada

Our understanding of and control over molecular adsorption on silicon has advanced very significantly in the last several years. It is now possible to provide a microscopic picture of structure and bonding in covalently attached molecule-silicon surface systems. This detailed understanding of adsorbate-surface structures was entirely lacking when the first wave of enthusiasm for molecular devices crested roughly 20 years ago. While many ideas for molecule-scale devices have been put forward in the past, the tools - both synthetic and analytical - to pursue those ideas did not exist. Now, the control necessary to begin exploring ways to incorporate organic function into existing technologies or, eventually, to make new molecule-scale devices is within reach.@footnote 1@ Experimental and modeling methods have emerged that effectively extend the resolution of STM to see the details of adsorbed molecule structure and bonding. In the next several years it is now realistic to expect structures and concepts dreamed about for decades to begin to be realized. This talk will focus on a self-directed growth process for creating molecular nanostructures on silicon.@footnote 2@ @FootnoteText@ @footnote 1@ Controlled Molecular Adsorption on Si: Laying a Foundation for Molecular Devices, R.A. Wolkow, Annual Review of Physical Chemistry, volume 50, 413-41, 1999. @footnote 2@ Self-Directed Growth of Molecular Nano-Structures on Silicon, G.P Lopinski, D.D.M. Wayner and R.A. Wolkow, Nature in press.

3:00pm **NS+NANO6+SS+MC-TuA4 Control of Spatial Distribution of Self-Assembled Diacetylene Compounds by Co-deposition with Fatty Acid Molecules*, Y. Kuwahara,*** *G.-M. Zhang, J.-W. Wu, M. Akai-Kasaya, A. Saito, M. Aono,* Osaka University, Japan

Control of self-assembled surface structure of functional organic molecules has been attracting intensive interest from a viewpoint of future applications such as novel material structures for nanometer-scale molecular devices. We have investigated self-assembled surface structures of two different chain organic molecules co-adsorbed on HOPG by use of scanning tunneling microscopy. The subject molecule was 10,12-tricosadiynoic acid, which is one of the diacetylene compounds possessing the possibility of being polymerized into macromolecular wire and/or sheet, and several kinds of fatty acids were used as buffer molecules. We used Langmuir Blodgett method for the fabrication of the molecular monolayers. In order to achieve the parallel molecular arrangement, the surface pressure for the deposition was deliberately controlled much lower than the saturate pressure and the substrate was horizontally oriented. A variety of molecular patterns inside the two-component monolayers were revealed, which could be briefly grouped into 'phase separation pattern', where microscopically pure 10,12-tricosadiynoic acid and fatty acid were observable respectively, and 'alternative pattern', in which the lamellae of the two sorts of molecules emerged alternatively. In order to evaluate the mechanism for the two dimensional surface ordering, we have also done the ab-initio molecular orbital calculation and the proposed structural model of the surface self-assembly is in good agreement with the theoretical simulations. Consequently, the possibility of controlling the spatial distribution of the diacetylene compounds on the solid surface has been demonstrated.

3:20pm **NS+NANO6+SS+MC-TuA5 The Interaction of Metal Atoms with Self-assembled Organic Monolayers***, **A.V. Walker**, B.C. Haynie, N. Winograd,* The Pennsylvania State University

Organic monolayers show great promise as materials for a wide range of technological applications. An understanding of the nature of the metal atom - organic monolayer interaction is vital in the development of molecular electronic devices. Recently it was demonstrated that deposited Al atoms can penetrate through an n-alkyl monolayer to the monolayer / Au (111) interface. This phenomenon is believed to occur via thermally activated transient defects in the monolayer. In this paper, we explore the thermodynamics of this system using time-of-flight secondary-ion-mass-spectrometry (TOF SIMS) and demonstrate that at low temperatures the rate Al atom penetration into the monolayer is reduced. We have also studied the interaction between other promising molecular wire candidates and metal atoms.

3:40pm **NS+NANO6+SS+MC-TuA6 Chiral Surface Reconstruction by Largish Molecules***, **M. Schunack**, L. Petersen, A. Kühnle, E. Laegsgaard, I. Steensgard, F. Besenbacher,* University of Aarhus, Denmark

Temperature-controlled scanning tunneling microscopy studies provide insight into the bonding, ordering and mobility of large organic molecules at metal surfaces. This is illustrated by investigations of disc-like molecules on a Cu(110) surface with a variable temperature STM, which can be operated down to 25 K.@footnote 1@ Hexa-tert-butyl decacyclene (HtBDC) self-assembles upon deposition onto Cu(110) above 250 K and forms a double-row structure in two directions surrounded by fast-diffusing single molecules. Nano-manipulation experiments with the STM at low temperatures revealed an underlying chiral reconstruction of the Cu surface. This consists of holes of approximately 14 Cu atoms pulled out of the surface. Surprisingly, the observed reconstruction is chiral. By gently annealing of the molecule structure at higher coverages, large enantiomerical pure domains with two different orientations build up. By means of simple effective medium theory calculations, we estimate the lower bound of the adsorption energy to be E@sub ad@ = 0.45 eV, and can give a plausible explanation for the observed structure. @FootnoteText@ @footnote 1@ L. Petersen, M. Schunack et al., submitted to Review of Scientific Instruments.

4:00pm **NS+NANO6+SS+MC-TuA7 From Functionalisation of Single Molecules to Self-organisation of Nano-structured Thin Films***, **Q. Guo**,* University of Birmingham, U.K. **INVITED**

The combination of functionalisation of individual molecules with self-organisation of the molecules into functional structures is a promising route for the fabrication of nanoscale electronic and optoelectronic devices. In this talk I will present experimental findings of nanostructured thin films prepared using this method. The dependence of the structure of molecular monolayers on the functionality of individual molecules will be demonstrated using chemisorbed acetate and benzoate species on TiO@sub 2@ surfaces as an example. Both acetate and benzoate attach to the substrate through strong bonding between the carboxyl end of the molecules and the metal cations at the surface of TiO@sub 2@. In the case of benzoate, the phenyl ring offers an extra functionality for intermolecular linkage, leading to the formation of dimerised rows of benzoate. Self assembled monolayers (SAMs) of functionalised alkanethiols adsorbed on Au(111) surfaces will also be discussed. Functionalisation of the tail group of thiol molecules gives rise to SAMs with different surface energies, allowing the fine tuning of the reactivity of the surfaces towards binding of deposited atoms and molecules. The formation of nano-particles of gold on carboxyl terminated SAMs has been investigated using scanning tunnelling microscopy (STM) and electron energy loss spectroscopy(EELS) and results will be presented to demonstrate the important role of functionality of individual molecules on nano-structure formation.

4:40pm **NS+NANO6+SS+MC-TuA9 Ion Beam Assisted Self-Organization of Periodic Nanowire-Arrays on CaF2 Substrates***, **M. Batzill**[1], F. Bardou, K.J. Snowdon,* University of Newcastle, UK

The fabrication of well ordered nanowire arrays over large areas is a challenge with many potential applications. Here we report a novel glancing incidence ion beam assisted self-organisation approach to form periodic wire-arrays over large areas on a CaF2(111) substrate. Preferential erosion of fluorine by the ion beam creates a surface enriched in calcium. The calcium self-organises in elongated island structures of preferential width and separation. If the sample is irradiated along a fixed azimuth we observe formation of nanowires with ~10 nm periodicity and wire lengths of at least several micrometers oriented along the azimuthal direction of ion beam incidence. Electrical conductivity measurements reveal a three order of magnitude lower conductivity normal to the wires than along the wires.

5:00pm **NS+NANO6+SS+MC-TuA10 Quantum Engineering of a Pb Nanostructure: Controlling the Thickness with Monolayer Precision***, **C.-S. Jiang**, H.-B. Yu, X.-D. Wang, C.-K. Shih,* University of Texas at Austin

We report a novel quantum engineering of Pb mesas on Si(111), designing the quantum number (N) of the electron resonator of Pb by modifying its thickness with monolayer precision. Pb deposition on Si(111) forms mesas on the surface, and the mesas serve as electron resonators because of the strong quantization along the surface normal direction. To modify the mesas into desired thickness, mass-transfer was first triggered by an STM-tip under controlled conditions. The triggering lead to the formation of single layer with annular shape at the edge of the mesa by transferring the Pb mass from the wetting layer. Once triggered, the mass transfer from the wetting layer to the top of the mesa continue until the new layer involving millions of atoms is completed. Once this layer is completed, no more mass transfer is observed unless a new triggering is performed. Each triggering leads to addition of one complete monolayer on top of the plateau. Using this process, the Pb mesa thickness can be engineered in a quantized fashion. Detailed mechanisms involved in the engineering will be discussed.

Photonics
Room 310 - Session PH-TuA
Challenges in Photonics Materials and Device Processing

Moderator: V. Teal, Lucent Technologies

2:00pm **PH-TuA1 From Integrated Optics to MOEMS at LETI , the Key Role of Plasma Processes***, **J.M. Margail**, P.B.M. Brunet-Manquat, C.C. Chabrol, T.E. Enot, M.J. Jadot, P.N. Noel, G.G. Grand, E.O. Ollier, P.M. Mottier,* CEA/LETI, France **INVITED**

Integrated Optics on Silicon, so-called IOS, started to be studied in France in 1973. In the early eighties the Laboratoire d'Electronique, de Technologie et d'Instrumentation (LETI), mainly focused in optical sensor development and worked to set up a photonic technology based on plasma processing (deposition and etching) of silicon oxide and nitride. During this period, IOS technology grew in maturity, strongly pushed forward by the increasing demand for optical fiber-based telecommunications. Today, low price optical passive components are targeted using microelectronic based processes and mass production. However one of the key issues for low price devices is the connection to optical fibers (pigtailing). It is estimated that pigtailing represents 80 percent of the component price. To overcome this problem, LETI introduced so called U-grooves formation for passive fiber alignment. This was performed by the application of silicon micro machining, using isotropic plasma etching of silicon. This introduction, during the second part of the eighties of silicon micro machining in the Integrated Optics group at LETI, opened the route to Optical MEMS (Micro-Electro-Mechanical-Systems) development. Today the strong demand concerning Optical Telecommunication pushed strongly forward the development of Optical MEMS and particularly optical microswitches devices for "fully optical" information routing. This paper will focus on the use of plasma processes for photonic device processing, it will be presented and illustrated (key issues, performances) by some examples of fabricated photonic devices as WDM Phasar, passive alignment of 1 to 8 dividers,1 to 8 optical microswitches.

2:40pm **PH-TuA3 Optical Properties of Tantalum Oxide Films Produced by High Density Plasma Enhanced Chemical Vapor Deposition***, **J.B.O. Caughman**, D.B. Beach, G.E. Jellison, Jr.,* Oak Ridge National Laboratory

Tantalum oxide films are being studied for use as waveguides for optical interconnect applications. The films have been deposited using a plasma enhanced CVD process using a high density inductively coupled plasma source. The inductively coupled source operates at 13.56 MHz and couples power to the plasma via a flat spiral coil. An oxygen plasma is produced in the ionization region and a tantalum containing precursor is injected downstream. The plasma produces atomic oxygen that interacts with the precursor in the gas phase as well as at the surface of the growing film. The deposition rate varies as the plasma coupling makes the transition from predominantly capacitive coupling to inductive coupling, which is related to the amount of atomic oxygen being produced. Gas phase composition is being determined by in-situ mass spectroscopy, and the optical properties of the films are being determined by using spectroscopic ellipsometry.

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[1] **NSTD Student Award Finalist**

Typical films have a bandgap of 4.3 eV and a refractive index of 2.19. The relationship between atomic oxygen production and films properties will be presented.

3:00pm **PH-TuA4 Processing of (Pb,La)(Zr,Ti)O@sub 3@ Waveguide Devices on Nb-doped SrTiO@sub 3@ by Solid-phase Epitaxy***, **K. Nashimoto**, H. Moriyama, K. Haga, M. Watanabe, E. Osakabe, S. Nakamura, T. Morikawa,* Fuji Xerox Co., Ltd., Japan **INVITED**

It is very attractive to utilize (Pb,La)(Zr,Ti)O@sub 3@ (PLZT) ferroelectric materials for optical waveguide devices because of their excellent electro-optic properties. It is also of great interest to fabricate an electrode/ferroelectric waveguide/electrode structure since a narrow electrode gap resulting in a low-voltage drive will be achieved as compared with conventional LiNbO@sub 3@ waveguide devices which have coplanar electrodes. For realizing the structure, epitaxial PLZT thin films are able to be grown on Nb-doped SrTiO@sub 3@ (Nb:ST) semiconductor substrates. However, it has been difficult to prepare a low-loss PLZT waveguides by vapor phase growth techniques. While, we demonstrated the growth of a heterostructure waveguide consisted of a PZT waveguide layer and a PLZT buffer layer on a Nb:ST substrate by solid-phase epitaxy. The PLZT buffer layer was introduced to avoid absorption loss by the substrate. The solid-phase epitaxy is a simple and useful process in terms of stoichiometric composition control, uniform large-area fabrication, low-loss capability, and waveguide patterning. The substrates were spin-coated with methoxyethoxide precursor solutions, preannealed to form amorphous thin films, and annealed to promote the solid-phase epitaxial crystallization of the thin films. The propagation loss in the grown epitaxial PLZT heterostructure waveguides was less than 1 dB/cm. Effective electro-optic coefficients as large as 40 pm/V and polarization insensitive properties were confirmed. A simple wet-etching process followed by the solid-phase epitaxy was developed for making 5 µm-wide channels in the PLZT waveguides. Digital matrix switches fabricated by the wet-etching and the solid-phase epitaxy showed low propagation losses and low-voltage responses.

3:40pm **PH-TuA6 Comparison of Dry and Wet Etch Processes for SiO@sub 2@/TiO@sub 2@ Distributed Bragg Reflectors for Vertical Cavity Surface Emitting Lasers***, **G. Dang**, H. Cho, K.P. Lee, S.J. Pearton,* University of Florida*; S.N.G. Chu, J. Lapata, W.S. Hobson,* Bell Labs, Lucent Technologies*; F. Ren,* University of Florida

Vertical-Cavity Surface Emitting Lasers (VCSELs) have generated much interest in the photonic devices field. They show tremendous promise for commercial applications involving optical fiber wave-guiding and optoelectronic integrated circuits. The semiconductor-based distributed Bragg reflector (DBR) and dielectric mirror are commonly used in VCSELs. We demonstrated a dry etch process of fabricating SiO@sub 2@/TiO@sub 2@ distributed Bragg reflector for 850 and 980 nm vertical cavity surface emitting lasers. The etchings was conducted with an inductively coupled plasma system. Both SF@sub 6@/Ar and Cl@sub 2@/Ar based etching chemistries were investigated. Very slow etch rates were obtained for TiO@sub 2@ by using Cl@sub 2@/Ar chemistry due to the low volatility of etch products, TiCl@sub x@. Using SF@sub 6@/Ar based chemistry, similar etch rates of TiO@sub 2@ and SiO@sub 2@ were obtained which is desired for alternating SiO@sub 2@/TiO@sub 2@ layers etching. An average etch rate of 1200 Å/min was achieved at ICP and rf power of 500 and 245W, respectively. Wet chemical etch processing was also explored using buffered oxide etchant and diluted HF. Etch rates of 1200 and 2000 Å/min in dilute HF solution were obtained for TiO@sub 2@ and SiO@sub 2@, respectively. However, a significant etch-undercut of the structure and delamination at the SiO@sub 2@/TiO@sub 2@ interfaces were observed with the wet chemical etching due the internal stress between the SiO@sub 2@/TiO@sub 2@ layers.

4:00pm **PH-TuA7 Advances in Materials and Design of Optical Amplifiers***, **D.J. DiGiovanni**,* Bell Laboratories, Lucent Technologies **INVITED**

To meet the explosion in demand for capacity, communications systems are increasing bandwidth and performance. The performance of optical amplifiers, the enabling component of these systems, must be extended through fiber design and operation to support this explosion. Even greater capacity can be realized using other gain media, such as Raman amplifiers. This talk will discuss EDF design issues and progress in Raman amplification. An EDFA consists of a length of silica optical fiber whose core is doped with several hundred ppm Er. Population inversion achieved using diode laser pumping at either 1480 nm or 980 nm provides gain to an optical signal around 1530nm. Signals of many wavelengths can be amplified simultaneously allowing up to 160 wavelength channels to pass over a single fiber. This allows tremendous increases in capacity as channel counts increase. The C-band EDFA (1530-1565nm) is ubiquitous and is being augmented with L-band amps (1565 to 1610nm). One of the most critical amplifier characteristics is uniformity of gain and noise over the spectral window of the amplifier. Glass hosts such as fluorides and tellurites can provide more uniform gain but face many technical difficulties. The low loss window of silica extends from 1300 to 1600 nm, significantly broader than the gain region of EDFAs. Rare earth substitutes to erbium have had limited success, though Tm-doped amplifiers look promising. The most successful approach by far is the use of Raman amplification, in which pump powers of about one Watt generate gain over several kilometers of fiber through scattering from optical phonons. Raman amplifiers have been demonstrated at many wavelengths and offer great promise as discrete amps or in combination with EDFAs. Gain can also occur within the transmission fiber itself, reducing noise and increasing capacity and reach. Next generation systems must employ Raman amplification to continue to grow capacity.

4:40pm **PH-TuA9 A Roadmap for Integrated Microphotonics***, **L.C. Kimerling**,* MIT Microphotonics Center **INVITED**

Low cost, high reliability and high functionality are the driving forces for on-chip circuit integration. Photonics has created a breakthough technology for high capacity information delivery over long distances. However, this technology has been implemented in a discrete point-to-point architecture that is reminiscent of the electronic ancestors of today's microelectronic chips. The need for integrated microphotonics is driven from two sources: 1) interconnection bottleneck that limits integrated circuit speed, and 2) all optical networking for the global distribution of information to finer network tributaries. The key components of the emerging roadmap for microphotonic integration are as follows. What are the appropriate architectures that deliver the full advantages of optics rather than emulate the electronics heritage? What devices will become the standard microphotonic circuit components? What are the materials systems and fabrication processes on which the new integrated microphotonics industry infrastructure will be built? This talk will outline the current view of the emergence of microphotonics and the near term challenges to its implementation as a global smart interconnection paradigm.

Plasma Science and Technology
Room 311 - Session PS2-TuA

Plasma Diagnostics I

Moderator: T. Tatsumi, Association of Super-Advanced Electronics Technologies (ASET)

2:00pm **PS2-TuA1 Effect of Xenon Dilution on Fluorocarbon Plasma Chemistry and Electron Distribution Function***, **H. Sugai**, T. Ishijima, M. Ikeda,* Nagoya University, Japan

Two types of unmagnetized high-density fluorocarbon plasmas, ICP (inductively coupled plasma, 13.56 MHz) and SWP (surface wave plasma, 2.45 GHz), are produced and compared in an identical vessel under the same gas conditions (10 % C@sub 4@F@sub 8@ + 90 % Ar, total pressure 20 mTorr). The ion and radical compositions are measured by a quadrupole mass spectrometer. The measurements at the same electron density of 2.5 x 10@super 11@ cm@super -3@ reveal that the ICP is more strongly dissociated than the SWP, with the smaller ratio of CF@sub x@ radical density to F radical density. Such different plasma chemistry between the two plasmas is attributed to the difference in the electron distribution functions (EDFs) observed in the experiment. Namely, the ICP has the EDF close to Maxwellian with higher electron temperature while the SWP has a bi-Maxwellian type of EDF composed of a cold electron group (lower temperature T@sub ec@) and a hot electron group (higher temperature T@sub eh@). The bi-Maxwellian EDF might be formed by stochastic heating at the plasma resonance layer in the SWP. Furthermore, replacement of the argon buffer gas with xenon gives rise to dramatic changes in plasma properties as follows. First, the xenon dilution makes it possible to obtain the same electron density by a factor of five less discharge power. Second, the radical density ratio of CF@sub x@ to F is increased by an order of magnitude in the Xe dilution, compared with the Ar dilution. Thirdly, the EDF measurement showed the value of T@sub ec@ lower by a factor of 2/3 in case of the Xe dilution. Finally, a global model of particle balance based on the measured EDFs supports these observations.

2:20pm **PS2-TuA2 Comprehensive Measurements of Neutral and Ion Number Densities, Neutral Temperature, and EEDF in a CF@sub 4@ ICP***, H. Singh, J.W. Coburn, D.B. Graves,* University of California at Berkeley

We present comprehensive measurements of the neutral number densities, ion number densities, neutral temperature, and the electron energy distribution function in a CF4 inductively coupled plasma at pressures between 1 and 30 mTorr, and deposited powers between 150 and 550 W. High degrees of dissociation are observed at the lower pressures. We believe this is a result of the large electron temperature (5-9 eV) at the lower pressures. The measurements of all the dominant radical and stable neutral species using appearance potential mass spectrometry allows the estimation of the neutral temperature at the neutral sampling aperture. The neutral temperature is also estimated from the change in the number density of a trace amount of argon added to CF4 when the plasma is turned on. Neutral temperatures up to 925 K are measured at the sampling aperture. The increase in neutral temperature with power at a constant pressure results in a decrease in the total neutral number density at a constant pressure. The electron temperature is sensitive to the neutral number density, especially at low densities. This leads to a significant increase in the electron temperature with power, resulting in the higher degrees of dissociation observed at low pressures. The number densities of radicals and their corresponding ions are generally strongly correlated in the plasma. We show evidence for a large surface loss coefficients for C and CF radicals.

2:40pm **PS2-TuA3 Planar Laser-Induced Fluorescence Investigation of Fluorocarbon Plasmas***, **K.L. Steffens**, M.A. Sobolewski,* National Institute of Standards and Technology **INVITED**

Fluorocarbon plasmas are extensively used in the semiconductor industry for etching and chamber-cleaning applications. The etching process involves a competition between substrate removal and deposition of a fluorocarbon polymer layer on the wafer surface. The CF@sub 2@ radical is thought to be a major participant in the formation of this polymer layer either directly or by forming gas phase precursors which deposit to form the layer. Thus, measurements of the CF@sub 2@ radical are crucial to the understanding of etching chemistries. In this work, the planar laser-induced fluorescence (PLIF) technique was used to measure two-dimensional images of CF@sub 2@ density in CF@sub 4@ and C@sub 2@F@sub 6@ plasmas in the capacitively-coupled Gaseous Electronics Conference rf Reference Cell. Measurements were made at 200 mTorr with power deposited in the plasma ranging from 30 to 150 W, both without a substrate and with a Si wafer present, in pure fluorocarbon and in oxygen/fluorocarbon mixtures. In addition to the PLIF images, we obtained broadband emission images, which indicate the regions where reactive species are formed in the gas phase, and measurements of the rf current and voltage at the electrodes. The spatial distribution of CF@sub 2@ is observed to go through a transition as power is increased, becoming more radially-uniform at higher powers. In addition, the presence of the wafer was found to have a strong effect on the CF@sub 2@ by both increasing the CF@sub 2@ density and affecting the spatial distribution. The addition of O@sub 2@ decreases the CF@sub 2@ density even in the presence of a wafer. Comparisons will also be made with previous studies in 100 - 1000 mTorr O@sub 2@/C@sub 2@F@sub 6@ and O@sub 2@/CF@sub 4@ chamber-cleaning plasmas. The results of this study will help to elucidate the role of CF@sub 2@ in fluorocarbon plasmas as well as provide data for development and validation of plasma simulations.

3:20pm **PS2-TuA5 Determination of Electron Temperature, Fluorine Concentration, and Gas Temperature in Fluorocarbon/Argon Plasmas using Optical Emission Spectroscopy***, **M. Schabel**, V.M. Donnelly, A. Kornblit, W. Tai, F. Klemens,* Lucent Technologies, Bell Laboratories

Recent advances in the interpretation of optical emission spectra from plasmas has made it possible to measure parameters such as electron temperature (T@sub e@), relative electron density, and gas temperature (T@sub g@) with this nonintrusive technique. This allows for the characterization and real-time monitoring of plasmas under conditions where the use of Langmuir probes is difficult (i.e. deposition plasmas or in manufacturing). Here we discuss the application of several advanced optical emission techniques to characterize fluorocarbon/Ar plasmas in an Applied Materials IPS inductively-coupled reactor. We have employed trace rare gas optical emission spectroscopy (TRG-OES), optical actinometry, and N2 vibrational spectroscopy to determine T@sub e@, fluorine atom concentration, and T@sub g@ respectively. Two etching processes, containing mixtures of Ar, C@sub 2@F@sub 6@, and C@sub 4@F@sub 8@, were evaluated as a function of pressure (5-90 mTorr). In the case of TRG-OES and optical actinometry, a mixture containing equal parts of He, Ne, Ar, Kr, and Xe (~1% ea.) was added. Large partial pressures of Ar prevent its use in TRG-OES because of radiation trapping effects (only the Kr and Xe lines were used to determine T@sub e@). Above 40 mTorr, T@sub e@ is insensitive to variations in pressure, and is ~2.5 eV. Below 40 mTorr, T@sub e@ increases with a decrease in pressure to 7 eV at 5 mTorr. The relative fluorine concentration increases with pressure and with the fraction of fluorocarbon species in the gas. At 5 mTorr, T@sub g@ is ~1010 K. Finally, we evaluated the effect of replacing Ar in the process gas with He or Ne, thereby allowing for the emission of the added Ar to be included with the Kr and Xe lines for determining T@sub e@. The resulting change in the accuracy of T@sub e@ measured by TRG-OES will be discussed in addition to how the use of He or Ne affects T@sub e@ and the relative electron density.

3:40pm **PS2-TuA6 Time-Resolved Measurements of Fluorocarbon Radical Concentrations during Pulsed Oxide Etching Plasmas***, **T.M. Bauer**, X. Wu,* University of New Mexico*; J.L. Cecchi,* University of New Mexico, US

We have measured the time evolution of the concentrations of the fluorocarbon radical precursors, CF@sub 2@ and CF, in pulsed plasmas using oxide etching chemistries. These measurements were performed in an inductively coupled plasma (ICP) reactor with a CHF3/Ar feedstock. We have explored a range of ICP powers of 300 to 900 W and a range of total pressure from 10 to 30 mTorr. The concentrations of CF@sub 2@ and CF, were measured with a wavelength-modulated diode laser spectroscopy system, modified to provide data with a time resolution of less than 0.3 ms. The pulse repetition rate and duty factor were varied to explore the full range of CF@sub 2@ CF and kinetics. Following the initiation of the plasma, [CF] increases in a nearly first-order manner. The behavior of [CF@sub 2@] is more complicated. Under pulsing conditions where [CF@sub 2@] remains nonzero for the entire period, there is an initial, very rapid (< 3 ms) decrease in [CF@sub 2@], indicating an enhanced loss, followed by a slower rise to equilibrium. After the termination of the plasma, [CF@sub 2@] shows a rapid increase, followed by an exponential decay. [CF] shows only an exponential decrease. The time constant for [CF@sub 2@] decay is in the range of 0.08-0.20 s, while the time constants for [CF] are more than a factor of ten smaller. Both time constants decrease with increasing pressure, and show a much smaller dependence on ICP power. We interpret our measurements with simple kinetic models and have extracted kinetic parameters during both the plasma pulse and after plasma termination.

4:00pm **PS2-TuA7 Development of an Instrument: Resonantly Enhanced Multiphoton Ionization of Radicals Detected Using Time of Flight Mass Spectrometry***, **W.C. Flory**, K.L. Williams, E.R. Fisher,* Colorado State University

Plasma deposition and etching mechanisms have been studied extensively in recent years due to the technological utility of low-temperature plasmas. Much remains to be done on a molecular level, however, before a complete understanding of the underlying chemistry is gained. To this end, we have designed and constructed a molecular beam apparatus employing resonantly enhanced multiphoton ionization (REMPI) to examine the production and reactivity of radical species in low temperature plasmas. This newly constructed plasma molecular beam apparatus builds on our past experiments employing laser-induced fluorescence (LIF) to study the surface reactivity of plasma radicals. The REMPI instrument has been employed to study SiF radicals produced in a SiF@sub 4@ plasma. The SiF radicals are detected using [2+1] REMPI combined with time of flight mass spectrometry (TOFMS). The absorption band from the (1,0) C@super"2@@SIGMA@@super+@ <-- X@super2@@PI@@sub1/2@ transition of the SiF molecule was monitored. Production of SiF in the plasma has been measured as a function of plasma parameters, including addition of H@sub2@ and O@sub2@, and applied rf power. In addition to results for SiF, comparisons will be made to fluorocarbon radicals (CF, CF@sub3@) and to other silicon-containing species (e.g. SiH@sub2@, SiH@sub3@). Preliminary results from these systems will be presented.

4:20pm **PS2-TuA8 Temperature and Distance Dependencies of Fluorocarbon Species Desorbed from Polymer Deposited Metal Surface in C@sub 4@F@sub 8@ Inductively Coupled Plasma***, **H.-H. Doh**,* University of Tokyo, Japan*; T. Ichiki,* Toyo University, Japan*; Y. Tezuka, Y. Horiike,* University of Tokyo, Japan

To investigate the interaction between chamber wall and fluorocarbon plasmas, various fluorocarbon species such as CF@sub x@ (x=1-3) and C@sub 2@F@sub 4@, C@sub 3@F@sub 5@ emitted from the polymer coated copper stage has been measured by in-situ in C@sub 4@F@sub 8@ inductively coupled plasma using quadrupole mass analyzer (QMA) for the temperature of the stage, the distance between the QMA orifice and the stage. The QMA and hot stage are installed around the center of the chamber and the temperature of chamber wall can be controlled with water cooling system. The copper stage is equipped with heating rod, externally forced nitrogen blowing and can be movable with the radial direction. When we measured the radical density at the distance between hot stage and the orifice over 10 mm at 10 mT of pressure and 500 W of RF power, the results did not show any effect from hot stage and the densities of CF, CF@sub 2@, CF@sub 3@ have an order of 10@super 13@/cm@super 3@, 10@super 13@/cm@super 3@, 10@super 12@/cm@super 3@ respectively. At the distance below 10 mm, however, all radical densities increase and the behavior of CF@sub 3@ radical shows the biggest change with the decrease of the distance. Next, at the distance of 3 mm, the change of radical density with the surface temperature from 50 to 300 ° C was investigated. The density of CF@sub 2@ and CF@sub 3@ decrease slightly up to 100 ° C and 170 ° C, respectively then increase continuously to 300 ° C. The CF@sub 3@ radical density changed also dramatically with the temperature. It goes up to 7x10@super 14@/cm@super 3@ at the surface temperature of 300 ° C. It suggests that the pressure or the number of density around the hot wall is high locally. The increased number of density is due to the emitted species from the hot wall and consists of CF@sub 3@ mostly. It is considered that the surface plays both roles of sink and source of radicals for its temperature and CF@sub 3@ radical is the dominant species emitted from the hot wall inferred from the results measured at 3 mm of the distance with the variation of the surface temperature.

4:40pm **PS2-TuA9 C@sub x@H@sub y@ Radical Measurements using Cavity Ring Down Spectroscopy in a Remote Ar/C@sub 2@H@sub 2@ Plasma**, ***M.C.M. van de Sanden,*** Eindhoven University of Technology, The Netherlands; *K.Y. Letourneur,* Eindhoven University of Technology, The Netherlands, Netherlands; *M.G.H. Boogaarts,* Eindhoven University of Technology, The Netherlands; *D.C. Schram,* Eindhoven University of Technology, The Netherlands, Netherlands

The ground state densities of C@sub x@H@sub y@ (x = 1,2, y = 0, 1) radicals in a remote Ar-C@sub 2@H@sub 2@ plasma used for high rate deposition of hard hydrogenated amorphous carbon films (a-C:H, rates up to 500 Å/s) have been investigated in detail by cavity ring down absorption spectroscopy (CRDS). Both C@sub 2@ and CH could be spectroscopically identified and measured as function of C@sub 2@H@sub 2@ gas flow admixture. From previous studies we deduced that the main dissociation products of C@sub 2@H@sub 2@ dissociation in our remote plasma is C@sub 2@H and H. In an attempt to measure the ground state density of C@sub 2@H we looked for a spectroscopic signature in the 260-280 nm region where Laser Induced Fluorescence measurements of ground state C@sub 2@H have been reported. No clear spectroscopic fingerprint of C@sub 2@H@sub 2@ could be measured although a clear broadband absorption is observed. The absence of a fingerprint of the C@sub 2@H radical could be due to the limited spectral resolution (0.7 cm@sup -1@) of the laser system used. Another plausible reason could be the hostile plasma environment (including formation of clusters) which influences the formation process of C@sub 2@H to such an extend (in terms of excitation of rovibrational and electronic states) that broadband absorption results. However, the broadband absorption measured as function of the C@sub 2@H@sub 2@ gas flow admixture shows trends we expect from the C@sub 2@H radical. In an attempt to resolve the problems faced we have designed an experiment in which we measure the C@sub 2@H radical using simultaneously threshold ionization mass spectrometry and cavity ring down spectroscopy. First results of these experiments will be presented.

5:00pm **PS2-TuA10 Electron Energy Control in Large-Diameter Inductively Coupled Plasma for High Performance of Etching**, ***T. Urayama***, *T. Tsurumi,* Tokai University, Japan; *Y. Horiike,* The University of Tokyo, Japan; *S. Fujii,* ADTEC Co., Ltd., Japan; *H. Shindo,* Tokai University, Japan

A method of electron energy control was studied in an inductively coupled plasma of a large diameter employing the multimode antenna, for high performance in device fabrication etching plasma processes. In etching plasmas, the electrons are prone to be excessively energetic in high density plasmas generated at low pressures. In SiO2/Si selective etching, for example, the high etching selectivity has been hardly realized under high etch rate, and this is understood as the radical density is too much low compared with the ion density. This happens eventually because the electron energy becomes too high at low pressures. The experiment was carried out in an inductively coupled plasma which was produced in a stainless-steel chamber of 350 mm in diameter by supplying the RF power of 13.56 MHz through the quartz window at one end. The electron energy could be reduced by changing the azimuthal mode of one-turn antenna from m=0 to m=2 with no notable change in electron density. The electron energy reduction was found higher in the higher mode and essential at low pressures by Langmuir probe measurement. These behaviors were also confirmed by optical emission spectroscopy. The method was extended to two-loop antenna with different diameters which enabled us to make the radial mode as well as the azimuthal mode. It was verified that these two-loop antenna with the modes could imporove the radial uniformity as well as the electron energy reduction, and a physical sputter etch rate of Si showed 5% radial uniformity in 12 ich area. It was concluded that the electron free path divided by the induction field reverse distance was the essential parameter in electron energy control.

Semiconductors
Room 306 - Session SC+EL+OF-TuA

Organic Chemistry on Semiconductor Surfaces

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

2:00pm **SC+EL+OF-TuA1 Novel Reactions of Organic Molecules for Controlled Modification of Semiconductor Surfaces**, ***D.J. Doren,*** University of Delaware **INVITED**

Recent theoretical work on reactions of organic molecules with semiconductor surfaces will be described. The focus will be on several mechanisms that allow molecules to react with low activation barriers on (100) surfaces of Si, Ge and diamond. Cycloaddition reactions are the most thoroughly understood reactions of organic molecules on these surfaces, having been studied extensively by both theory and experiment. This work has established several families of molecules that readily chemisorb. However, in several cases, there are competing side reactions. The origins of this competition, and some approaches to controlling selectivity tbrough the choice of precursor molecule, will be discussed. Finally, a reaction that attaches an organic molecule to the surface by dissociation (as opposed to cycloaddition) will be described.

2:40pm **SC+EL+OF-TuA3 Peter Mark Memorial Award Address**, ***S.F. Bent***[1], Stanford University **INVITED**

Tailoring the surface properties of semiconductor materials through organic modification is one means of providing new functionality to the semiconductor surface, incorporating properties such as passivation, lubrication, optical response, molecular recognition, or biocompatibility. Chemical modification also has tremendous utility for the controlled synthesis of organic/semiconductor interfaces for numerous electronic and optical applications, including the coupling of organic-based devices to silicon-based microchip technology. In this presentation, I will discuss different organic attachment strategies used to functionalize semiconductor surfaces in a dry processing environment. Unsaturated molecules, such as alkenes or dienes, can be attached by cycloaddition reaction across the Si-Si dimer at the Si(100)-2x1 surface; the reaction occurs at the surfaces of Ge and diamond, as well. Amine groups provide another reactive functionality for surface attachment. The relative reactivities of cycloaddition, N-H bond dissociation, and nitrogen lone pair interactions at the Si(100)-2x1 surface will be described using a series of pyrrole compounds. The use of protecting groups to manipulate the surface reaction pathway will be demonstrated. The potential for these different classes of attachment reactions to impact future applications will also be discussed.

3:20pm **SC+EL+OF-TuA5 Structure of Cyclopentene Adsorbed on InP (001)-(2x1) Surface**, ***Q. Fu***, *C.H. Li, D.C. Law, M.J. Begarney, R.F. Hicks,* University of California, Los Angeles

It has been a growing interest in engineering ordered, defect free organic thin films on semiconductor substrates for the next generation miniature electronic devices. Using metalorganic vapor phase epitaxy, we have successfully grown indium phosphide (2x1) surface terminated with a complete layer of phosphorous dimers. On InP (2x1) surface, a dangling bond on each phosphorous dimer is filled with a single electron, which makes it an ideal substrate for growing organic films through reactions with @pi@-bond of unsaturated molecules. Here, we have characterized the molecular structure of cyclopentene adsorbed on the InP (2x1) surface by scanning tunneling microscopy, internal-reflectance infrared spectroscopy, reflectance difference spectroscopy, and molecular cluster calculations. It is

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

found that the exposed phosphorous dimers are the adsorption sites for the unsaturated organic molecule. Two adsorption configurations were identified: one with the C@sub 5@H@sub 8@ molecule sitting on top of a P dimer, and another one with the C@sub 5@H@sub 8@ molecule bridging across two neighboring P dimers. At the meeting, we will present a comparison of cyclopentene adsorption characteristics on InP (001)-(2x1) versus Si (100)-(2x1).

3:40pm **SC+EL+OF-TuA6 Formation and Reaction of Organic Layers on Germanium: Reaction of 1,5-cyclooctadiene with the Ge(100) Surface***, P. Prayongpan, D.S. Stripe,* ***C.M. Greenlief,*** University of Missouri, Columbia

Organic alkenes can bond to Ge(100) surfaces to produce monolayer organic films that are chemically homogeneous and structurally ordered. The bonding of these molecules to the Ge(100)-(2x1) reconstructed surface is analogous to a class of ring-forming reactions known in organic chemistry as [2+2] cycloaddition reactions. While the bulk reactions involve the reaction of two alkene groups to form a four-member ring, the analogous surface reaction involves two electrons from the organic alkene and two electrons from the surface Ge=Ge dimers. Here, the formation of ordered organic layers on Ge(100) substrates is examined by the reaction of 1,5-cycloocatadiene with Ge(100). This molecule reacts with the Ge dimers leading to a [2+2] cycloaddition reaction product. A combination of ab initio calculations and surface sensitive experimental techniques are used to probe the interactions. Surface modification of the organic layers is also explored. The reaction of the organic layers with atomic hydrogen and a series of alcohols will be discussed.

4:00pm **SC+EL+OF-TuA7 A Comparative Study of the Bonding of N-Containing Heterocyclic Molecules to the Si(001) Surface***,* ***X. Cao****, S.K. Coulter, H. Liu, J. Liu, R.J. Hamers,* University of Wisconsin, Madison

Recent studies of a variety of unsaturated hydrocarbons has lead to increased interest in understanding the factors controlling bonding of more complex organic molecules to silicon surfaces. By understanding the propensity for heterocyclic molecules to bond into various possible configurations, we are able to gain insight into the factors controlling selectivity in molecule-surface bonding. We have studied the adsorption of pyrrole and its partially-unsaturated analog, 3-pyrroline, onto the Si(001)-(2x1) surface using Fourier-transform infrared spectroscopy, X-ray photoelectron spectroscopy, and scanning tunneling microscopy (STM). At 300 K, XPS spectra of pyrrole show a single, sharp N(1s) level, while FTIR spectra show that the molecule retains the high-frequency peaks that are characteristic of aromatic molecules; isotropic labeling studies show that attachment occurs through the N atom via cleavage of the N-H bond. These results show that pyrrole retains its aromatic character after bonding to the surface. In contrast, XPS and FTIR data for 3-pyrolline shows that it can bond through the N atoms or through its C=C bond via the surface equivalent of a [2+2] cycloaddition reaction. This study shows that molecules with aromatic rings show a strong preference for retention of this aromaticity, while molecules without aromaticity have more diverse chemical bonding configurations. Implications for understanding the attachment of other N-containing molecules to surfaces will be discussed.

4:20pm **SC+EL+OF-TuA8 Reaction of Pyrrole and Pyrrole Derivatives on Si(100)-2x1***,* ***G.T. Wang****, C. Mui, C.B. Musgrave, S.F. Bent,* Stanford University

The ability to covalently bond to semiconductor surfaces organic layers with custom-tailored functionality could have applications in a number of areas, including lithography, molecular electronics, sensors, and low k dielectric materials. Previous studies have shown that the Si(100)-2x1 surface dimer can react with unsaturated hydrocarbons, forming covalently bound [4+2] Diels-Alder and [2+2] cycloaddition products at the surface. Amines have shown promise as alternative candidates for layer-by-layer growth and the model amine ammonia is known to react with silicon via N-H dissociation across the surface dimer. The use of more complex amines for surface modification requires an understanding of how various functional groups in the amine affect its reactivity and bonding configuration with the surface. In this study, the interaction of pyrrole and pyrrole derivatives, including saturated and unsaturated secondary and tertiary amines, with the Si(100)-2x1 surface under ultra-high vacuum is investigated via multiple internal reflection infrared spectroscopy, Auger electron spectroscopy, temperature programmed desorption studies, and ab initio quantum chemistry calculations. The results show that the nitrogen lone pair plays an important role in the reaction of amines with the Si(100) surface. In particular, the stable room temperature molecular adsorption of methylpyrrolidine through its lone pair is permitted due to the presence of a protecting methyl group, while its unprotected analogue, pyrrolidine, proceeds to covalently bond to the surface through N-H dissociation. Additionally, results examining the reaction of the Si(100) surface with a model amide (N-methylacetamide), which contains both carbonyl and amine functionalities through a peptide unit and hence could serve as a bifunctional unit for layer-by-layer growth, are presented.

4:40pm **SC+EL+OF-TuA9 Attaching Aromatic Molecules to the Si(001) Surface via Oxygen and Sulfur Tethers***,* ***S.K. Coulter****, M.P. Schwartz, J. Liu, R.J. Hamers,* University of Wisconsin, Madison

Phenol, benzenethiol and phenyl disulfide have been used as model systems to compare the bonding of chemically-similar aromatic molecules to the Si(001)-2x1 surface through different Group VI tethers. The behavior of these substituted aromatic hydrocarbons on the Si(001) surface has been investigated using Fourier transform Infrared Spectroscopy (FTIR), X-ray Photoelectron Spectroscopy (XPS) and Scanning Tunneling Microscopy (STM). Both FTIR and XPS indicate that phenyl disulfide bonds exclusively through the sulfur substituent groups. Phenol and benzenethiol molecules bond predominately through their oxygen/sulfur substituent groups, although a small minority may chemisorb on the surface via ring attachment. Thermal studies indicate that the molecules attached to the surface via sulfur or oxygen tethers are stable to temperatures above 550 K. STM studies show that these molecules attach directly to the silicon dimer and, in the case of phenyl disulfide, form ordered rows of aromatic rings.

5:00pm **SC+EL+OF-TuA10 Chemical Reactions on the Diamond(100) Surface: First-principles Theory and Comparisons to Experiment***,* ***D.R. Fitzgerald****, D.J. Doren,* University of Delaware

Density functional theory calculations have been used to investigate the structures, energetics, and reaction pathways of the [4+2] and [2+2] cycloaddition reactions of butadiene with the C(100)-2x1 surface. One-dimer and three-dimer cluster models were used to represent the surface. Vibrational spectra of the product species were also calculated. Activation free energies suggest that the [4+2], or Diels-Alder mechanism, will be kinetically favored. The presence of adjacent unreacted surface dimers affects the orientation of the cycloaddition product. The adsorption of hydrogen on the surface has also been studied. Cluster size is seen to have a large effect on the vibrational spectrum of the adsorbed hydrogen. Theoretical results are compared to recent experiments.

Surface Engineering
Room 201 - Session SE-TuA

Surface Engineering: Surface Preparation to Postcoating Surface Finishing

Moderator: Y.-W. Chung, Northwestern University

2:00pm **SE-TuA1 Surface Engineering by Plasma Immersion Ion Processing***,* ***M.A. Nastasi,*** Los Alamos National Laboratory **INVITED**

Ion beam processing, including ion implantation and ion beam assisted deposition (IBAD), are established surface modification techniques which have been used successfully to synthesize materials for a wide variety of tribological applications. In spite of the flexibility and promise of the technique, ion beam processing has been considered too expensive for mass production applications. However, an emerging technology, Plasma Immersion Ion Processing (PIIP), has the potential of overcoming these limitations to become an economically viable tool for mass industrial applications. In PIIP, targets are placed directly in a plasma and then pulse biased to produce a non-line-of-sight process for intricate target geometries without complicated fixturing. If the bias is a relatively high negative potential (20-100kV) ion implantation will result. At lower voltages (50-1200V), deposition occurs. Potential applications for PIIP are in low-value-added products such as tools used in manufacturing, orthopedic devices, and the production of optical coatings. This talk will focus on the technology and materials science associated with PIIP.

2:40pm **SE-TuA3 The Surface Modification of Wear Resistant HSS Cutting Tools with Adapting Engineered Coatings***,* ***G.S. Fox-Rabinovich,*** McMaster University, Canada*; A.I. Kovalev,* SPRG, Russia

The friction parameter, wear resistance, phase and chemical compositions, atomic structure of multi-layered surface engineered coating for cutting tools were studied. A number of fine structure analysis methods including AES, SIMS, EELS, EELFS were applied. The surface engineered coatings being investigated was formed by duplex surface treatment technology including ion nitriding of high-speed steel and by hard PVD (Ti, Cr) N coating cathode arc deposition. Top protective layer of the multi-layer coating was formed by lubricant coating consists of Perfluoro-popyethers (PFPEs) with hydroxyl end groups (known by the brand name Z-DOL). This lubricant has the following chemical structure: (HO-CH2-CF2)-(C2F4O)6-(CF2O)290-CF2-CH2OH. Evolution of atomic structure at PFPE was investigated by vibration spectroscopy. Such adapting coating makes it possible significantly - by factor of 2.0-2.5 increase the wear resistance of cutting tools by surface damage prevention during running-in stage of wear. The mechanism of Z-DOL influence on wear phenomenon as a lubricant is discussed.

3:00pm **SE-TuA4 Enhanced Passivity of Austenitic AISI 304 Stainless Steel by Low-Temperature Ion Nitriding***, **S. Rudenja,*** Tallinn Technical University, Estonia*; I. Odnevall Wallinder, C. Leygraf,* Royal Institute of Technology, Sweden*; P. Kulu, V. Mikli,* Tallinn Technical University, Estonia

Low-temperature ion-nitriding introduces interstitial nitrogen into the austenitic stainless steel matrix. The passivity and anodic oxidation of a nitrided AISI 304 stainless steel have been studied by potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) in 0.1 M H@sub 2@SO@sub 4@ + 0.05 M HCl solution. The chemical composition of the oxidized surface film on the stainless steel was analyzed by X-ray photoelectron spectroscopy (XPS), including angle-resolved spectra of the elements. The distribution of the chemical elements beneath the oxide-metal interface was studied with Auger depth profiling. Defects of crystalline structure nearby the surface were studied with transmission electron microscopy (TEM). An enhanced passivity of the nitrided stainless steel was detected by anodic polarization. Capacitance measurements by EIS revealed a 3-4 nm thick oxide film on the surface of nitrided specimens, that is 2-3 times thicker than on blank specimens. XPS analyses and Auger depth profiles indicate increased chromium uptake into the oxide film on nitrided surface, supposedly through the kinetically stable oxide-metal interface enriched with nitrogen and nickel. Several possible mechanisms influencing passivation of the nitrided stainless steel may operate simultaneously. Among these mechanisms, austenite strengthening by interstitial nitrogen near the oxide/alloy interface and associating with structural defects like dislocation branches are most likely explanation for the enhanced passivity of the nitrided stainless steel.

3:20pm **SE-TuA5 CVD Diamond Nucleation under Extreme Conditions***, **K.-A. Feng,*** Institute of Physics, CAS, China*; J. Kang,* University of Michigan*; Z. Lin,* Institute of Physics, CAS, China

It is well known that the diamond is an outstanding material for a wide range of applications. The synthesis of the diamond films using various methods of CVD (chemical vapor deposition) have received significant in recent years. In order to enhance the density of diamond nucleation, abrading the substrate surface with diamond paste and adding negative bias to the substrate are two routine pretreatment methods. Here, we propose a new method to greatly enhance the nuclei density. Under extreme low pressure and ultra pure hydrogen, high-density nucleation of diamond is achieved on mirror-polished silicon in a hot-filament chemical vapor deposition (HFCVD). The diamond film are studied by Scanning Electron Microscopy (SEM) and Raman Spectrum. The enhanced nucleation at very low pressure should be attributed to an increased mean free path, which induces a high density of atomic hydrogen and hydrocarbon radicals near the silicon surface. Atomic hydrogen can effectively etch the oxide layer on the surface of silicon and so greatly enhance the nucleation density. The residual oxygen in the hydrogen (not ultra pure) is shown a very obvious negative effect on the nucleation of diamond, that is, oxygen atoms possess opposite effects in the nucleation stage and the growth stage of the diamond.

3:40pm **SE-TuA6 Large-area Nitrogen-doped SiO@sub 2@ Films Deposition in a Large-scale Integrated RF PSII/PVD System***, **L. Wu,** D. Manos,* College of William and Mary

A large-scale integrated implantation/deposition system was used to deposit large-area, high quality nitrogen-doped SiO@sub 2@ films. With a 0.61 m I.D. chamber, 0.57 m I.D. quartz window, and 0.43 m I.D. RF antenna, the system is capable of large-area, uniform surface materials processing. The nitrogen-doped SiO@sub 2@ films were produced by simultaneous sputter deposition of SiO@sub 2@ and nitrogen ion implantation by the plasma. At an RF power of 750 watts, the deposition rate of SiO@sub 2@ over an approximately 20 inch area was 5-10 Å/min. The films were characterized by AES and SIMS depth profiling, and variable angle spectroscopic ellipsometry (VASE). The films were highly transparent, with refractive indexes around 1.5 throughout the visible spectrum and zero extinction coefficients. The films were stoichiometric SiO@sub 2@ with an implanted nitrogen concentration of around 10%. The level of nitrogen doping is easily controllable by adjusting the implant pulse frequency and pulse voltage. N-doped SiO@sub 2@ films have been deposited on Si, Ti, and stainless steel substrates with good adhesion and uniformity. The nitrogen implantation improved properties of the interface between the film and the substrates. This method shows promise for depositing SiO@sub 2@ at low temperature, on a variety of substrates, allowing a range of dopant combinations to produce variable dielectric constants. The low-temperature process preserves small feature dimensions when performed on a masked substrate. The process was modeled using MAGIC and Profile Code to compare to the measured lateral and depth profiles of various features.

4:00pm **SE-TuA7 Cleaning, Etching and Oxidation of W films for Microelectronics Applications***, P. Cao, M.-S. Lim, S.S. Perry,* University of Houston*; **E.J. Mitchell**, D.C. Koeck, H.C. Galloway,* Southwest Texas State University

During the fabrication of integrated circuits with tungsten plugs, the tungsten surface undergoes chemical mechanical planarization (CMP). It is important to characterize the effects of any pre- or post-processing cleaning steps on the tungsten surface. To investigate this, we have examined tungsten films prepared by chemical vapor deposition (CVD) to carefully characterize how they respond to common cleaning and etching procedures. Topography changes were examined by atomic force microscopy and surface chemistry was characterized by X-ray photoelectron spectroscopy (XPS). Cleaning and etching procedures investigated in this study include solutions of KNO@sub 3@ and H@sub 2@O@sub 2@, KOH, a buffered solution of KIO@sub 3@ and NaOH as well as the RCA SC-1 clean. The relative ability of these cleaning treatments to remove residual hydrocarbons from the W surface has been evaluated. In addition, the influence of these treatments on the native tungsten oxide layer has been measured as well. The XPS results show a general increase in the oxidation state in W for most solutions, specifically entailing an increase in W@super 6+@ and a corresponding decrease in W@super 4+@. These results are relevant to both material removal during the CMP process and the effectiveness of cleaning procedures. A correlation of the results shows that weakly oxidizing solutions are not as effective in removing organic contaminants as strongly oxidizing solutions.

4:20pm **SE-TuA8 Reactions of Fluorocarbon Polyatomic Ions with Polymer Surfaces***, **M.B.J. Wijesundara**, L. Hanley,* University of Illinois at Chicago

25 - 100 eV, mass-selected CF@sub 3@@super +@ and C@sub 3@F@sub 5@@super +@ ions are used to deposit fluorocarbon films on polystyrene surfaces. Monochromatic x-ray photoelectron spectroscopy and contact angle measurements are used to quantify the effect of the unique chemistry and structure of the incident ions on the fluorocarbon film. Oxidation and other aging processes are also examined for these films, following air exposure for several weeks. Fluorination efficiency of the film increases with ion size and energy. The fluorocarbon components vary with ion size, energy, and fluence. These ions deposit largely intact at 25 eV and undergo partial decomposition at 50 or 100 eV. Overall, CF@sub 3@@super +@ and C@sub 3@F@sub 5@@super +@ behave as covalently bound polyatomic precursors or fragments that can react and become incorporated within the polystyrene surface. The size and structure of the ions affect polymer film formation via differing chemical structure, reactivity, sticking probabilities, and energy transfer to the surface. Overall, the different reactivity of these two ions with the polymer surface supports the argument that larger species contribute to the deposition of polymeric films from fluorocarbon plasmas. These results further indicate that complete understanding and accurate computer modeling of plasma-surface modification requires accurate measurement of the identities, number densities, and kinetic energies of higher mass ions and energetic neutrals.

4:40pm **SE-TuA9 An Aging Study of Fluorocarbon Plasma Polymers Deposited on Si-C Plasma Polymer Films Using XPS***, C.E. Moffitt, **D.M. Wieliczka**,* University of Missouri, Kansas City*; Q.S. Yu, C.M. Reddy, H.K. Yasuda,* University of Missouri, Columbia

Thin films (~<3nm) formed from D.C. plasma polymerization of C@sub 2@F@sub 6@ deposited on trimethylsilane-based D.C. plasma polymers have proven to tremendously enhance adhesion of subsequent organic coatings. This enhancement in adhesion was observed to be restricted to coatings deposited within the first 5 days after deposition. An XPS study of the aging of these films during exposure to atmosphere was carried out on polished aluminum alloy samples. It was ascertained that extended exposure to x-ray flux degraded the samples, so an optimized scheme was employed to limit the exposure and collect data quickly. The results of this time study indicate that a decrease in fluorine concentration correlates with the time frame of the decrease in adhesion promotion. The decrease in a high binding energy fluorine peak component is the dominant evolution of the fluorine spectra. This is accompanied by a decrease in CF@sub x@ levels and increases in C-C and C-CF bonding during the continued oxidation of the films. The thin nature of the films allows for the observation of the underlying silicon signal, which appears virtually unchanged throughout the oxidation process, indicating a stable interface with little change in the overlayer thickness. Partial support for this project was provided by DARPA under U.S. Air Force contract # AF F33615-96-C-5055.

5:00pm **SE-TuA10 An XPS Investigation into the Role of Oxygen in the Structural Formation of Methylated Silane Plasma Polymers***, **C.E. Moffitt**, D.M. Wieliczka,* University of Missouri, Kansas City*; T.M. El-Agez,* Islamic University of Gaza, Palestine*; Q.S. Yu, C.M. Reddy, H.K. Yasuda,* University of Missouri, Columbia

Films formed from plasma polymerization of carbon containing, silane-based monomers have shown great promise as intermediate adhesion and anti-corrosion promoters on a number of substrates. Incorporation of oxygen in the deposition process has been shown to modify the surface energy of deposited films, yielding a fully variable range of surface wettability from hydrophobic to hydrophilic. A photoemission investigation of films formed with several monomers and various plasma ignition techniques was carried out. It yields insight regarding the chemical changes at the interface with oxidized surfaces, the surface structure of post-deposition plasma treated films, and the mechanism responsible for elemental bonding changes between types of deposition. Aging of a D.C. trimethylsilane plasma polymer was observed to primarily involve the oxidation of Si sites with a loss of carbon bound to silicon sites, which is correlated to spectroscopic ellipsometry data indicating the tendency for a more silica type index of refraction as the film ages. The aging/oxidation study then further correlates to the observed effects of the incorporation of oxygen with the monomer during deposition. Partial support for this project was provided by DARPA under U.S. Air Force contract # AF F33615-96-C-5055.

Surface Science
Room 208 - Session SS1-TuA
Mechanisms and Control of Surface Reactions

Moderator: A.V. Teplyakov, University of Delaware

2:00pm **SS1-TuA1 Bestowing Chirality: The Ultimate Control of a Surface Reaction***, **R. Raval**,* University of Liverpool, UK **INVITED**

Enantioselective surface reactions represent the ultimate expression of selectivity in catalysis, involving stereodirecting processes where only one optical component of a product is formed. A case in point is the hydrogenation of b-ketoesters, which occurs readily on metal surfaces, but with no stereoselectivity so that both optical products are produced. However, catalytic studies show that this reaction pathway can be rigidly controlled if the metal is first modified by pre-adsorption of particular chiral molecules. But how is stereocontrol is achieved by the presence of these chiral modifiers?. Here, we report surface spectroscopic results from chirally modified metal surfaces created under controlled environments. We show that the adsorbed modifiers display rich and complex phase diagrams in which the chemical nature and 2-dimensional organisation of the chiral molecules is a dynamic function of surface coverage and temperature. Of particular interest is that at certain points of the phase diagram, extended supramolecular assemblies of the chiral molecules impose growth directions that destroy existing symmetry elements of the underlying metal and, thus, directly bestow chirality to the achiral metal surface! These supramolecular assemblies also create chiral channels and chiral spaces at the metal surface that we believe are responsible for imparting enantioselectivity by forcing the reactant molecules to dock in one particular orientation, which subsequently directs the hydrogen attack. Our work shows that it is possible to sustain a single chiral domain across an extended surface. The implications of creating structured chiral metal surfaces go beyond catalysis, with potential applications in molecular electronics, non-linear optics and molecular recognition, and we conside general principles which govern the expression of true extended chirality in 2-dimensional space.

2:40pm **SS1-TuA3 Artificial Control of Catalytic Functions for Reaction Selectivity by Thickness-extensional Mode Resonance Oscillation of Acoustic Wave***, **Y. Inoue**, Y. Yukawa, N. Saito, H. Nishiyama,* Nagaoka University of Technology, Japan

Thickness-extensional mode resonance oscillation (TERO) of bulk acoustic waves generated by a piezoelectric effect was applied to a 100 nm Ag or Pd film catalyst deposited on a positively polarized ferroelectric single crystal of z-cut LiNbO3 (z-LN), and the TERO effects on reaction selectivity of the catalyst surfaces were studied. For ethanol decomposition on Ag and Pd, TERO with a resonance frequency of 3.5MHz caused remarkable increases in ethylene production without changing acetaldehyde production. The increased activity decreased to an original low level with turning TERO off. Increases in selectivity for ethylene production with TERO were from 56 to 86% for Ag and 31 to 97% for Pd. The activation energy of ethylene production was lowered significantly by the TERO. For comparison, x-cut LiNbO3 (x-LN) having thickness-shear mode resonance oscillation (TSRO) was employed as a ferroelectric substrate, for which no significant activity enhancements for both ethylene and acetaldehyde production were observed with the resonance oscillation. Laser Doppler measurements showed that TERO caused large dynamic lattice displacement vertical to the surface. The surface potential and photoelectron emission behavior varied with the TERO. TERO has been shown to have influences on the work function of the catalyst surfaces, which permits to change the catalytic functions with selectivity.

3:00pm **SS1-TuA4 Surface Science Models of Sulfided NiW, CoW, NiMo and CoMo Hydrodesulfurization Catalysts***, L. Coulier, **G. Kishan**,* Eindhoven University of Technology, The Netherlands*; J.W. Niemantsverdriet,* Eindhoven University of Technology, The Netherlands, Netherlands

Industrial catalysts used in the hydrotreating of crude oil can successfully be modeled using silicon single crystals as the planar support for the catalytically relevant sulfides. Wet chemical deposition techniques on the basis of spin coating enable the preparation of these catalysts via industrially relevant chemistry. The catalytic behavior of these models in the desulfurization of thiophene to butenes has been measured in a batch reactor. Clear relations between the order in which the elements convert to sulfides and the catalytic activity have been observed: The key step in the preparation is to retard the sulfidation of Ni and Co with respect to that of Mo and W. To this end, stabilizing chelating agents may be added in the preparation stage.

3:20pm **SS1-TuA5 Chemistry of Thiophene, H@sub 2@S, and SO@sub 2@ on Carbide-Modified Mo(110) and Mo@sub 2@C Powders***, **J. Dvorak**, T. Jirsak, J.C. Hanson, J.A. Rodriguez,* Brookhaven National Laboratory

The most widely used catalysts in hydrodesulfurization (HDS) reactions consist of a mixture of cobalt and molybdenum sulfide on an alumina support. More stringent environmental legislations stress the need to develop a new generation of HDS catalysts that lead to the ultimate goal of clean burning fuels. Recently, it has been shown that molybdenum-carbide catalysts have the potential to replace sulfided Mo catalysts in industrial HDS reactors. We have investigated the chemistry of a series of S-containing molecules on carbide-modified Mo(110) [i.e. MoC@sub x@] and Mo@sub 2@C powders using synchrotron-based photoemission, x-ray absorption near-edge spectroscopy and time-resolved x-ray diffraction. Thiophene adsorbs molecularly on MoC@sub x@ at 100 K. By 200 K, upon desorption of the thiophene multilayer, chemisorbed thiophene and its decomposition products (S and C@sub x@H@sub y@ fragments) coexist on the MoC@sub x@ surface. At 250 K, no C-S bonds are left. H@sub 2@S and SO@sub 2@ are also very reactive on MoC@sub x@, with the cleavage of H-S and S-O bonds taking place at temperatures well below 300 K. For these systems, the chemistry observed on carbide-modified Mo(110) is quite similar to that seen on Mo@sub 2@C powders.

3:40pm **SS1-TuA6 Selective Surface Reactions of Single Crystal Metal Carbides: Alkene Production from Short Chain Alcohols on Titanium Carbide and Vanadium Carbide***, **R.L. Guenard**, L.C. Fernández-Torres, S.S. Perry,* University of Houston*; P. Fantz, S.V. Didziulis,* The Aerospace Corporation

The reaction of short chain alcohols on the (100) surface of single crystal vanadium carbide (VC) and titanium carbide (TiC) have been studied using temperature programmed desorption (TPD), high resolution electron energy loss spectroscopy (HREELS), and x-ray photoelectron spectroscopy (XPS). The short chain alcohols form an alkoxide upon adsorption at 153K on both VC(100) and TiC(100). The alkoxide intermediate selectively reacts with the carbides to produce an alkene and water. Specific isotopic labeling revealed @gamma@ C-H bond scission as a key step in alkene formation. A comparison of the TPD intensities of reaction products on both surfaces indicates that VC(100) has a higher reactivity towards alcohols, with an approximately four-fold higher reaction yield as compared to TiC(100). This difference in reactivity is accounted for by a difference in the electronic structure of these carbide surfaces. This study implicates potential pathways of lubricant degradation in tribological applications and highlights the possible need for passivating additives for carbides used in such applications.

4:00pm **SS1-TuA7 Alkylidenes on Molybdenum Carbide; Stable Carbenes on the Surface of a Catalytically Active Material**, *E.M. Zahidi, H. Oudghiri-Hassani,* ***P.H. McBreen,*** Laval University, Canada

Molybdenum carbide competes well with platinum and ruthenium as a catalyst for various hydrocarbon transformation reactions. This reactive material can activate both CC and CH bonds. Yet, the present study shows that it is possible to form a layer of thermally stable carbenes on the carbide surface. Dissociative chemisorption of ketones leads to the formation of surface alkylidene groups which are stable to above 900 K. Extensive RAIRS, photoemission and XPS results will be used to describe the mechanism for the formation of these groups, and to outline their stability and their high temperature surface chemistry. This novel method for coupling relatively complex organic species to reactive surfaces may find application in the preparation of tailored catalysts, such as chiral modified systems. The observation of surface alkylidenes is also of direct interest for heterogeneous metathesis chemistry.

4:20pm **SS1-TuA8 Radical Rearrangement as a Probe of Partial Oxidation Mechanisms: Reaction of (Bromomethyl)cyclopropane on Oxygen-Covered Mo(110)**, ***J.A. Levinson****, M.A. Sheehy, L.J. Deiner, I. Kretzschmar, C.M. Friend,* Harvard University

Rearrangement reactions were used to study the transient intermediates formed during partial oxidation on oxygen-covered (0.75 ML) Mo(110) surfaces using (bromomethyl)cyclopropane. Using temperature programmed reaction spectroscopy, a competition between desorption and reaction was observed, with 1,3-butadiene, butene, ethylene, water, and dihydrogen as reaction products; these were evolved between 450 and 600 K. No cyclic or three-carbon species were observed in the mass spectroscopic data. Two linear analogues, 4-bromo-1-butene and 3-buten-1-ol, were also studied and produced similar product spectra. Coadsorption experiments with deuterated species revealed that the hydrogen incorporated into butene and ethylene arises at the time of reaction from the reaction intermediate. Mass spectra indicated that there may be both alkyl and alkoxide species at the surface for the Br-containing compounds, as the hydrocarbon products are evolved at two temperatures. X-ray photoelectron spectroscopy experiments are in progress to determine the surface bonding and the temperature of C-Br bond scission. Fourier transform infrared spectroscopy was used to determine conformational and structural changes in the surface intermediates as a function of temperature. For (bromomethyl)cyclopropane, a double bond appears near 400 K. These data imply that a ring-opened intermediate forms following C-Br bond scission, which is then followed by H-elimination or incorporation. The use of isotopically labeled oxygen on Mo(110) revealed that the alkoxide species for the Br-compounds bind through surface oxygen, whereas the alcohol binds through its original hydroxyl group. Lowering reactant coverage reduces butene and butadiene formation and favors ethylene production. Variation of oxygen coverage from saturation to clean Mo(110) surfaces causes selective product formation to convert to non-selective decomposition.

4:40pm **SS1-TuA9 Reaction Kinetics on Supported Model Catalysts: A Molecular Beam / In-Situ IRAS Study of the CO Oxidation on Pd/Al@sub 2@O@sub 3@**, ***J. Libuda****, I. Meusel, J. Hoffmann, J. Hartmann, H.-J. Freund,* Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany

We have employed molecular beam techniques combined with time-resolved in-situ IR reflection absorption spectroscopy to study the CO oxidation kinetics on oxide-supported model catalysts. As model systems we have used Pd particles of different size and morphology grown under UHV conditions on a well-ordered alumina film on NiAl(110). Previously, these systems have been characterized in detail with respect to their geometric and electronic structure. Sticking coefficient measurements demonstrate that - contrary to what is observed for densely packed Pd single crystal surfaces - at room temperature and above the Pd crystallites rapidly incorporate a large amount of oxygen. This subsurface and bulk oxygen is not accessible to CO oxidation at low temperature. Once the bulk reservoir is saturated, stable oxidation rates are obtained. Taking advantage of the single-scattering conditions in a molecular beam experiment, we quantitatively address effects which are specific for supported metal catalysts, such as support mediated adsorption. Also, activation energies for the LH reaction step as a function of adsorbate coverage are derived. Various coverage regimes are considered, in particular the limiting cases of high CO or O coverage. The transient behavior and the steady-state CO@sub 2@ production rate are probed over a wide range of reactant fluxes and CO/oxygen flux ratios. In particular, we discuss the origin of the different transient behavior of the oxidation rate on supported Pd particles. Time-resolved IR absorption spectroscopy is employed during the reaction to monitor changes in the occupation of different adsorption sites in transient beam experiments and under steady-state conditions.

5:00pm **SS1-TuA10 Dissociative Chemisorption of Chloromethanes on Ir(110), Ir(111) and Oxygen Modified Ir(111)**, ***R.J. Meyer****, C.T. Reeves, D.J. Safarik, D.T. Allen, C.B. Mullins,* University of Texas at Austin

Chlorinated hydrocarbons are a primary component of the waste streams from the manufacture of many commodity chemicals. Noble metal catalysts, including iridium on alumina, have been shown to be active for both oxidative and reductive catalytic treatment methods. However, the causes of deactivation and mechanisms by which these reactions proceed are not precisely known. Dissociative chemisorption of CH@sub 3@Cl, CH@sub 2@Cl@sub 2@, CHCl@sub 3@, and CCl@sub 4@ on Ir(110) and Ir(111) has been examined at surface temperatures from 77-1200 K using molecular beam methods. From our ongoing studies two particularly exciting results have emerged. (1) We have identified the reactive site for methyl chloride on Ir(110). An examination of CH@sub 3@Cl on hydrogen precovered Ir(110) indicates that the reaction pathway for dissociative chemisorption can be shut off by filling the high temperature desorption state. This result implies that methyl chloride chemisorbs in the hollow site of the rows of the (110) surface. (2) The production of phosgene was observed when a CCl@sub 4@ beam was impinged on an oxygen modified Ir (111) surface. We propose that phosgene forms via a Langmuir-Hinshelwood mechanism from the reaction of absorbed oxygen with CCl@sub 2@ surface species formed during the decomposition of carbon tetrachloride. Competing reactions involving the oxidation of completely dissociated carbon tetrachloride become significant as the surface temperature increases. COCl@sub 2@ formation was maximized at an oxygen surface coverage of approximately 0.3 ML. At higher oxygen coverages, the production of phosgene decreases due to a diminished reactive adsorption of carbon tetrachloride but the efficiency of COCl@sub 2@ formation per dissociatively chemisorbed CCl@sub 4@ increases dramatically.

Surface Science
Room 209 - Session SS2-TuA
Stimulated Processes and Excitations

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

2:00pm **SS2-TuA1 Ultra-Fast Dynamics Measurements of One- and Two-Dimensional Surface State Electrons on Stepped Cu(775)**, *X.J. Shen, H. Kwak,* ***D. Mocuta****, S. Smadici, R.M. Osgood, Jr.,* Columbia University

Dynamical questions regarding surface state electrons on metallic surfaces can best be answered in the time domain using ultra-fast nonlinear probes. Of particular interest is the effect of controlled nano-size features on the femtosecond scale dynamics of surface states. In this connection, we have employed the momentum- and time-resolved two photon photoemission technique to study the dispersion and lifetimes of these states on a prototypical nano-structured surface, stepped Cu(775). Here we report on a newly observed one-dimensional surface state (0.27 eV below Fermi level) and an image-like unoccupied state on stepped Cu(775). Both states are dispersive along the step direction but are localized in the direction perpendicular to the steps. The origin of the states is attributed to the step-edge potential confinement and to an Anderson localization mechanism. The lifetime of n=1 electrons on the regular step array of Cu(775) has been measured as a function of their translational momentum, k@sub //@. At the terrace normal, this lifetime is equal to that for flat Cu(111), i.e., t = 16±2 fs. The lifetime decreases symmetrically with k@sub //@ about k@sub //@ = 0 for electrons moving parallel to the step orientation. This is in good agreement with a theoretical calculation of k@sub //@ dependent n=1 lifetime done on Cu(111) by Echenique, et al.@footnote 1@ In contrast, the lifetime is asymmetric in k@sub //@ for the direction perpendicular to the step edges. The asymmetric behavior is attributed to direction-dependent coupling between image and bulk states, leading to a decrease in lifetime of the electrons climbing the steps and an increase for descending electrons. The overlap between the unoccupied localized state and the n=1 image state at k@sub //@ = 0.2 Å@sup -1@ results in an increase in the measured lifetime at this value of the momentum. @FootnoteText@ @footnote 1@J. Osma, I. Sarria, E. V. Chulkov, J. M. Pitarke, and P. M. Echenique, Phys. Rev. B59, 10591 (1999).

2:20pm **SS2-TuA2 Electron-Stimulated Oxidation of Al(111)*, V. Zhukov*,** *I. Popova, J.T. Yates, Jr.,* University of Pittsburgh

The electron stimulated dissociative adsorption of O@sub 2@ on Al(111) has been studied at surface temperatures from 90 to 300 K. A rastering electron beam technique has been used to deliver electrons with energies from ~1 to 200 eV to the aluminum surface during O@sub 2@ exposure. Experimental evidence for the presence of an O@sub 2@ precursor was found for the oxidized Al(111) surface at low temperature. Precursor adsorption energy of 70-80 meV was estimated from the temperature variation of the oxide growth rate, stimulated by 100 eV electrons. The effect was found to be proportional to the primary beam current. A threshold electron energy of 7 ± 0.5 eV for the electron stimulated oxidation was observed when utilizing electrons with variable energies. This threshold value is in agreement with the 6.8 eV electron attachment cross-section resonance for the gaseous O@sub 2@ species. In contrast to the significant increase of oxidation rate on the oxide-precovered aluminum surface, no effect of electrons was found on the initial stages of oxide growth on the clean Al(111) surface over the temperature range studied. This suggests that the O@sub 2@ precursor is stabilized on oxide clusters.

2:40pm **SS2-TuA3 Ion-Influenced Nucleation and Surface Diffusion: A Computational Study*, Z. Wang*,** *E.R. Blomiley, E.G. Seebauer,* University of Illinois, Urbana-Champaign

Ion-beam assisted deposition (IBAD) has been used to improve material properties for a wide variety of semiconductors, metals and oxides. In many applications, beneficial effects derive from ion-induced surface diffusion, while deleterious effects derive from ion-induced damage to the substrate. Process optimization involves finding a kinetic balance between these opposing effects, which in turn demands useful rate expressions. We have recently demonstrated experimentally both the enhancement and inhibition of surface diffusion by low-energy ions in the case of Ge/Si(111). We have simulated this system via molecular dynamics, and have developed a fairly nuanced picture of the interplay between sputtering, knockin, and vacancy formation on the surface and within the bulk. Our simulations show marked thresholds for both ion energy and substrate temperature, with a previously unknown conservation law relating these two parameters: E + bT = constant. The physical significance of the proportionality constant b we derive is discussed. The ideas deriving from these simulations are then applied to continuum simulations of ion-influenced nucleation during IBAD, with the goal of explaining why ions sometimes increase nucleation densities and other times decrease them.

3:00pm **SS2-TuA4 Surface Modification of CaF@sub 2@ for Improved Heteroepitaxy*, A. Bostwick*,** *B.R. Schroeder, S. Meng,* University of Washington*; E. Rotenberg,* Lawrence Berkeley National Laboratory*; M.A. Olmstead,* University of Washington

Fluorite (CaF@sub 2@) is a candidate epitaxial insulator for three dimensional circuits. However, heteroepitaxial growth of semiconductors and metals on CaF@sub 2@(111) surfaces is inhibited by CaF@sub 2@s low surface energy. We have investigated use of electron irradiation and surfactant incorporation to alter the surface energy balance and promote laminar growth of silicon and related materials on CaF@sub 2@(111). We report here photoelectron diffraction studies of the interaction of electrons and arsenic with CaF@sub 2@(111) surfaces. Irradiation of CaF@sub 2@ with 40 eV electrons creates fluorine vacancies in the film, raising the fluorite surface energy. The resultant defects are extremely reactive. Exposure of this surface to arsenic passivates the surface to oxygen and water contamination. We find As@sub 4@ does not stick to pristine CaF@sub 2@(111) between room temperature and 600C, but sticks only in the presence of surface defects. Room temperature exposure results in As on the fluorite surface. At elevated temperature, however, arsenic diffuses into CaF@sub 2@. It occupies two ordered sites, neither of which is a bulk fluorine site. As-stabilized, irradiated CaF@sub 2@ is more stable than either pristine or irradiated CaF@sub 2@ with regard to photon-stimulated desorption of fluorine. Deposition of Si on unirradiated CaF@sub 2@ results in an amorphous film at room temperature, but sticking is inhibited at high temperature. Si deposition on As-terminated CaF@sub 2@, on the other hand, leads to laminar growth of Si at 550C. The As acts as a surfactant, floating to the top of the Si film.

3:20pm **SS2-TuA5 Consequences of Electron Irradiation of Hydrated Crystals: Self Organized Nanometer Cone Formation*, S.C. Langford*,** *M. Dawes, J.T. Dickinson,* Washington State University

Radiation effects on hydrated single crystals are poorly understood. We find that dense arrays of conical structures, with aspect ratios on the order of 200, are produced by exposing single crystal brushite (CaHPO@sub4@.2H@sub2@O) to energetic electrons (2 keV). By exposing thin brushite platelets bonded to the surface of a metal heater to energetic electrons, the surface temperature can be controlled independently of electron dose. This work shows that cone formation requires surface temperatures of 400-600 @degree@C. The cones are directed along the direction of the incident electrons, and often display a cap-like structure that may play a role in cone production. Cone formation is accompanied by the development of a distinctive orange luminescence during electron irradiation, presumable due to electronic defects. The waters of hydration in this material may play a role in cone development by enhancing ion mobility in the heated material. Characterization of surfaces covered with conical structures has been performed by TEM, EPS, and IR spectroscopy.

3:40pm **SS2-TuA6 Femtosecond Measurements of Surface-State-Electron Dynamics on Nanostructured Ni Surfaces*, S. Smadici*,** *X.J. Shen, D. Mocuta, R.M. Osgood, Jr.,* Columbia University

Ultra-fast nonlinear optical probes have recently been shown to enable time-resolved measurements of electron dynamics on metal surfaces. While most measurements have been on flat surfaces, we have recently begun an investigation of the ultra-fast dynamics for electrons confined in surface metallic nano-structures. Here we will describe our femtosecond, momentum- and time-resolved two-photon photoemission measurements of electron lifetimes and dispersion curves on systems with controlled nano-size features obtained by Ag deposition on stepped Ni(977) and Ni(111). Ag deposition reduces the Ni work function and permits the observation of surface and image states at the accessible pulse energies. We will present measurements of the dispersion for the occupied surface state and the unoccupied n=1 image state located ~3Å above the metal surface. We report on band-folding of the Ag induced surface state on Ni(977), with a controllable bandwidth, caused by the periodic step potential. As the Ag coverage is increased the width of the allowed band increases as predicted by a Krönig-Penney model which is appropriate to the periodic potential on this Ag-decorated surface. The n=1 state lifetime measurements on the Ag/Ni(977) system showed a downward trend with increasing parallel momentum. This result is similar to that observed by us on Cu surfaces@footnote 1@ and is consistent with theoretical results indicating the increased importance of elastic and inelastic scattering at higher k@sub //@. The n=0 surface state lifetime showed an unexpected similar behavior when moving away from the terrace normal direction with a variation of ~10 fs over a change of k@sub //@ of 0.2Å@super-1@. This result is explained in terms of a resonant excitation of the n=2 image state, with the detector sampling a mixture of two different photoemission channels. @FootnoteText@ @footnote 1@.X. J. Shen, H. Kwak, A. M. Radojevic, S. Smadici, D. Mocuta, and R.M. Osgood, Jr., submitted to Phys. Rev. Lett.

4:00pm **SS2-TuA7 Theory of Single Molecule Vibrational Spectroscopy and Microscopy*, N. Lorente*,** *M. Persson,* Chalmers/Gothenburg University, Sweden

A recent breakthrough in Surface Science has been the experiments demonstrating vibrational spectroscopy and microscopy of single molecules by inelastic electron tunneling using a scanning tunneling microscope.@footnote 1@ Based on density functional theory and a many-body generalization of Tersoff-Hamann theory, we have developed a theory and calculational method for this new spectroscopy.@footnote 2@ We apply our theory to acetylene on copper and explain why only the carbon-hydrogen stretch modes are observed in terms of elastic and inelastic contributions to the tunneling conductance. The calculated values for the changes in tunneling conductance induced by these stretch modes and their spatial images are in good agreement with experiments. We find that the symmetry of the adsorbate-induced states makes the inelastic signal for the anti-symmetric stretch mode to dominate over the signal for the symmetric one. This result is in agreement with experiment and shows that the symmetries of the lowest unoccupied molecular states has an important influence on the spatial dependence of the vibrationally inelastic tunneling.@footnote 3@ @FootnoteText@ @footnote 1@ B. C. Stipe, M.A. Rezaei, and W. Ho, Science 280, 1732 (1998). @footnote 2@ N.

Lorente and M. Persson, (submitted to Phys. Rev. Lett.). @footnote 3@ N. Lorente, M.Persson, L.J. Lauhon, and W. Ho, (to be submitted).

4:20pm **SS2-TuA8 Transient Currents as a Tribological Probe***, **J.V. Wasem**, S.C. Langford, J.T. Dickinson,* Washington State University

When conductors contact and slide on insulator surfaces charge transfer between the surfaces allows one to measure instantaneous transient currents (TC). We have instrumented a vacuum tribological apparatus with high sensitivity normal, lateral, and TC pick-up using metal and semiconductor stylii. Performing single pass wear track formation tests on polymer and ceramic substrates, we observe striking correlations between the mechanical and electrical signals. In particular, the TC exhibit fluctuations with a rich temporal/frequency spectrum, for example during stick-slip events. Through correlations with SEM images of the substrate we are able to relate spatial microscopic damage and corresponding TC behavior. The TC reveals details of the micromechanics during wear on microsecond time scales. Studies on Fomblin Zdol lubricated hard drive surfaces reveals charge transfer events that correspond to free electrons going to the lubricant. Yates et al. have previously shown that electron attachment to such polyperfluoroethers can cause decomposition of the polymer. Thus, our studies can provide quantitative values and rates for the charge deposited which can then be used to predict lubricant lifetimes from measured attachment cross-sections.

Surface Science
Room 210 - Session SS3-TuA
Water/Surface Interactions

Moderator: E.M. Stuve, University of Washington

2:00pm **SS3-TuA1 Alumina-Water Interactions from First Principles***, **K.C. Hass**, W.F. Schneider, C.M. Wolverton,* Ford Motor Company **INVITED**

The chemical formula for aluminas is often written explicitly as Al@sub 2@O@sub 3@@sup .@nH@sub 2@O to emphasize the key role that water plays in this important class of materials. To date, there is little microscopic understanding of this role, despite its clear relevance to fields ranging from catalysis, corrosion, and adhesion to geology, microelectronics, and atmospheric chemistry. This talk will summarize recent progress on two aspects of this problem: (1) the hydroxylation of @alpha@-Al@sub 2@O@sub 3@ (0001)@footnote 1@, and (2) the bulk structure and phase stability of @gamma@- and other transitional aluminas that are produced by the dehydration of boehmite (@gamma@-AlOOH). Both studies are based on accurate planewave pseudopotential, density functional theory methods. Comparisons to related recent work and future prospects and challenges will also be discussed. @FootnoteText@ @footnote 1@ K. C. Hass, W. F. Schneider, A. Curioni, and W. Andreoni, Science 282 (1998) 265, and to appear in J. Phys. Chem. (2000).

2:40pm **SS3-TuA3 The Effect of Boron on Water Dissociation and Surface Diffusion of Atomic Hydrogen on Single Crystal Ni@sub3@(Al, Ti) (110)***, **J. Wang**, Y.-W. Chung,* Northwestern University

Polycrystalline Ni@sub3@Al alloys are severely embrittled in a moist environment at room temperature. Ductility measurements showed that addition of boron suppresses this moisture-induced embrittlement. Previous results indicated that water dissociates on clean Ni@sub3@(Al, Ti) (100) and (110), resulting in hydrogen evolution at ~350 and 400 K respectively. To explore the effect of boron on water dissociation, we first dosed the surface of clean Ni@sub3@(Al, Ti) (110) with controlled amounts of boron, using a specially designed low-energy negative boron ion source, followed by low-temperature exposure to D@sub2@O. The interaction between water vapor and boron-modified Ni@sub3@(Al, Ti) (110) was investigated using temperature-programmed desorption, X-ray photoemission and Auger electron spectroscopy. Auger and X-ray photoemission studies on boron-modified Ni@sub3@(Al, Ti) (110) show that boron reacts with water to form hydroxyls at 130~190 K. Hydrogen desorption occurs at ~950 K from boron-modified Ni@sub3@(Al, Ti) (110), indicating strong B-H bonding. After water dosing at ~130 K, the surface diffusion coefficients of atomic hydrogen on clean and boron-modified Ni@sub3@(Al, Ti) (110) surfaces were measured at 270 K with electron stimulated desorption. The surface diffusion of atomic hydrogen on 0.05 monolayer boron-modified surface is about 10 times slower than that on clean boron-free surface. Therefore, the strong B-H bonding suppresses both hydrogen desorption and the surface diffusion of atomic hydrogen to the crack tip at room temperature. These results may explain the suppression of moisture-induced embrittlement of Ni@sub3@Al and related alloys by boron.

3:00pm **SS3-TuA4 Physicochemical Properties of Water and Ammonia Ice Thin Films***, **D.J. Safarik**, R.J. Meyer, C.T. Reeves, C.B. Mullins,* University of Texas at Austin

We have studied the physical and chemical properties of water and ammonia ice films utilizing surface science techniques. Ultrathin films of amorphous solid water (ASW) and crystalline ammonia ice were grown via supersonic molecular beam on an Ir(111) substrate and characterized with temperature programmed desorption (TPD) and low energy electron diffraction (LEED). Overlayers of ASW dramatically alter the desorption of ammonia, resulting in a TPD spectrum that is distinctly different than free ammonia desorption yet unlike the desorption of carbon tetrachloride through water overlayers (the "molecular volcano") as reported by Smith et al.@footnote 1@ Whereas uncovered ammonia multilayers desorb with zero order kinetics at approximately 100 K, covered films desorb in a sequence of one to three distinct and rapid bursts. The number of ammonia releases, the temperature at which they occur, and their intensity varies with the thickness of both the ASW and ammonia ice films. These phenomena cannot be completely explained by a diffusional model. The overlying water film desorbs with zero order kinetics at approximately 160 K, apparently unaffected by the ammonia discharge. However, TPD, isothermal desorption, and LEED experiments indicate that the ammonia underlayer accelerates the kinetics of ASW crystallization and reduces the volatility of the remaining solid water. @FootnoteText@ @footnote 1@ R. S. Smith, C. Huang, E. K. L. Wong, and B. D. Kay. The Molecular Volcano: Abrupt CCl4 Desorption Driven by the Crystallization of Amorphous Solid Water. Phys. Rev. Lett. 79, 909-912 (1997).

3:20pm **SS3-TuA5 Water Ion Cluster Formation in High Electric Fields at and Near a Pt Emitter Tip***, **C.J. Rothfuss**, V.K. Medvedev, E.M. Stuve,* University of Washington

Water ion cluster formation in high electric fields has been characterized on a field cleaned Pt emitter tip over temperatures ranging from 110K to 300K. The ion clusters were mass resolved using either an ExB filter or time of flight mass spectroscopy, or imaged directly using Field Ion Microscopy (FIM). Experimental results explain the qualitative trends observed in previous studies of this nature. For H@super +@(H@sub 2@O)@sub n@ cluster formation, the onset potential was found to be dependent upon the value of n and is lower for large masses. This dependency follows from a consideration of the thermodynamics of dissociative ion formation and proton solvation by nearby water molecules. However, the formation of large clusters is entropically unfavorable at high temperatures for low concentrations of water molecules on the surface and dynamically unfavorable at low temperatures. As a result high local concentrations and surface mobility are needed for creation of large n clusters. This local concentration has been experimentally imaged on the surface using FIM, under conditions favoring large n cluster formation, but is absent in the direct field ionization of water (H@sub 2@O@super +@) in space near the surface. With increasing field, each successive (n-->n-1) cluster becomes energetically accessible and becomes the dominant species due to its kinetic advantage. Above the condensation point for water on Pt (~165K), the limiting factor for determining the maximum n in field adsorbed cluster formation is the surface residence time of the water. As temperature increases, the residence time decreases and the propensity for forming large n clusters diminishes. Activation energies for ion cluster desorption were found to be 0.85 eV, 0.76 eV and 0.55 eV for n=3, 4 and 5, respectively. Below the condensation point, surface diffusion limits the supply function for large cluster formation, so lower temperatures result in decreased ion signal for large n clusters.

3:40pm **SS3-TuA6 Interactions of Methanol with Water and Hydrogen in Electrolytic Adlayers on Pt(111)***, **D.S.W. Lim**, E.M. Stuve,* University of Washington

To model the interactions of methanol with water and hydrogen at electrolye/electrode interface, thermal desorption experiments of the co-adsorbed system were performed on Pt(111). In electrochemical environments, adsorption of methanol on Pt(111) is inhibited by chemisorbed hydrogen, and water competes with methanol for available Pt sites. In ultra-high vacuum, methanol desorbed from Pt(111) in a multilayer state B@sub m@ at 142 and a monolayer state A@sub m1@ at 180 K. However, when the surface was pre-adsorbed with hydrogen, the desorption temperature of the methanol monolayer state, A@sub m1@, was lowered by as much as 20 K. The reduction in desorption temperatures was attribited to weakened interactions between methanol and the surface due to chemisorbed hydrogen. When methanol was co-adsorbed with water, mutual displacement between the methanol monolayer and water bilayer occurred on the surface. Water molecules in direct contact with Pt(111) surface form bilayer structure that desorbs at 173 - 178 K. A realistic simulation of the electrolytic adlayers was to co-adsorb all three species: methanol, water and hydrogen on Pt(111). In a water-lean adlayer system, the methanol monolayer state was destabilized by chemisorbed hydrogen. However, with the introduction of a sufficient amount of water, methanol was re-stabilized and, the effects of hydrogen-induced destabilization were completely erased when excess water was added to the adlayer. Methanol behaved as if it was only interacting with water. The results of these experiments illustrate that there is a delicate balance of hydrogen-induced destabilization and water-promoted stabilization in the electrolytic adlayers on Pt(111), and behavior of methanol interactions with co-adsorbed hydrogen and water followed that observed in electrochemical environments.

4:00pm **SS3-TuA7 From Gases to Dust: Ice Chemistry in the Interstellar Environment***,* ***H.J. Fraser,*** University of Nottingham, UK, NL*; M.R.S. McCoustra,* University of Nottingham, UK*; D.A. Williams,* University College London, UK

It has become clear in the last decade that gas-phase reaction schemes cannot soley account for the variety and richness of chemistry in the Interstellar Medium (ISM). In such environments, gas-dust interactions play a key role. In dense molecular regions, H@sub 2@O is the most abundant ice: it is vital to understand the freeze out, reactivity and desorption processes of atomic and molecular species on such ice surfaces to fully evaluate the chemical evolution of the ISM. A novel surface science experiment has been constructed that simulates the harsh conditions in the ISM. Traditional surface science techniques such as TPD and RAIRS have been combined with a Quartz Crystal Microbalance sample stage, capable of operating below 10 K. The experiment is equipped to study several aspects of the gas-dust interaction that are central to astrophysics, measuring sticking probabilities and rates of desorption empirically and accurately, as well as identifying the nature of the surface bound states. We will present the first results from this experiment, characterising a number of thin molecular ice films prepared under a variety of conditions to reflect a range of substrate morphologies. We will report measurements of the interaction of simple molecular species with these H@sub 2@O ices, concentrating on the behaviour of such systems between 10 and 150 K. The implications of these results to the chemistry and astrophysics of the ISM will be mentioned.

4:20pm **SS3-TuA8 Diffusion of Organic Molecules in Ice Measured Using Laser Resonant Desorption Depth-Profiling***,* ***F.E. Livingston,*** *S.M. George,* University of Colorado

Knowledge of the diffusion of organic molecules in ice is important for understanding the history of the Earth's atmosphere preserved in ice cores. Molecular diffusion in ice is affected by chemical and physical properties such as hydrophilicity, size and geometry. To explore these properties, we have measured the diffusion rates of different organic molecules such as carboxylic acids and alcohols. Diffusion was measured using an infrared laser resonant desorption (LRD) technique to depth-profile into the ice. LRD was accomplished using a Q-switched Er:YAG laser that emits light at @lambda@=2.94 µm. The laser radiation is resonantly absorbed by the O-H stretching vibration of H@sub2@O molecules and thermalized to facilitate desorption in the surface region. We have employed LRD depth-profiling to study the diffusion kinetics of formic (HCOOH) and acetic (CH@sub3@COOH) acid. LRD analysis revealed that acetic acid diffuses ~3 times faster than formic acid. The diffusion coefficients for formic acid vary from D~2 x10@super-13@ cm@super2@/s at T=175 K to D~2x10@super-10@ cm@super2@/s at T=195 K. Arrhenius analysis yielded a diffusion activation energy of E@subA@~24 kcal/mol and a diffusion preexponential D@subo@~4x10@super16@ cm@super2@/s. For acetic acid, the measured diffusion coefficients range from D~7x10@super-13@ cm@super2@/s at T=170 K to D~7x10@super-10@ cm@super2@/s at T=195 K. Arrhenius analysis yielded diffusion kinetic parameters of E@subA@~18 kcal/mol and D@subo@~1x10@super11@ cm@super2@/s. The faster diffusion for acetic acid argues that the lower hydrophilicity and larger size of acetic acid does not reduce its diffusion relative to formic acid.

4:40pm **SS3-TuA9 Can Clustering Lower the Barrier to Dissociation of Water on Nickel Surfaces?***, L. Mao,* ***K. Griffiths,*** *P.R. Norton,* University of Western Ontario, Canada

The interaction of water with Ni(110) surface has been extensively explored in this group due to its fundamental and practical importance in the fields of heterogeneous catalysis, electrochemistry as well as corrosion. At temperatures ï€¤ 400K, water molecules react rapidly with Ni(110) producing adsorbed O and H2(g). Reaction probabilities can reach as high as 0.24 and our studies indicate that the reaction mechanism involves single water molecules. Dissociation of water can also occur at low temperatures (ï€£220K) provided that we begin with an adsorbed chemisorbed layer. The activation energy for the dissociation reaction is believed to be lowered by some means which involves a cluster of at least two water molecules. The exact mechanism is still speculative at this stage. Between these two temperatures, the Ni surface appears to be inert towards the dissociation of water. Under normal UHV dosing conditions, the surface is sufficiently hot to prevent an appreciable dynamic coverage of dimers. At the same time, the activation energy barrier for the unimolecular , high temperature mechanism cannot be overcome. The aim of this study is to investigate the reaction between water and Ni(110) in this >inert= temperature regime. In this study, we have produced locally relatively high pressures at the surface using a capillary doser to demonstrate that there is a non-linear dependence of reaction rate on dosing pressure. The absolute number of impinged water molecules as well as the instantaneous coverage of water (governed by the dosing pressure) determines the extent of reaction.

5:00pm **SS3-TuA10 Surface and Near Surface Reactions in Aqueous Solution Exposed Na@sub 2@O-Al@sub 2@O@sub3@-SiO@sub 2@ Glasses***,* ***V. Shutthanandan,*** *S. Thevuthasan, D.R. Baer, J.P. Icenhower, M.H. Engelhard, B.P. McGrail,* Pacific Northwest National Laboratory

Glass and ceramic waste forms are proposed for the stabilization and immobilization of nuclear wastes. Recent findings show that Na ion exchange reaction control the release of radionuclides from the glass matrix. As part of understanding the processes leading to sodium release and ion exchange, the surface and near surface reaction regions on several specimens of Na@sub 2@O-Al@sub 2@O@sub 3@-SiO@sub 2@ glasses with fixed Na@sub 2@O and variable Al@sub 2@O@sub 3@ (10 mole % and 15 mole %) concentrations have been examined after exposures to isotopicaly labeled aqueous D@sub 2@@super 18@O solutions. The sodium removal and the deuterium and oxygen uptake in the glass samples were measured using Rutherford backscattering spectrometry (RBS), X-ray photoelectron spectroscopy (XPS) and nuclear reaction analysis (NRA). The results show that the Na exchange rate is much higher than the matrix dissolution rate. Although the sodium concentration is decreased in the near surface region, it is not totally removed from the outer surface. In this same region, there is also a significant amount of @super 18@O incorporated demonstrating considerable interaction between the water and the glass. On the basis of the depth distributions of Na, D and @super 18@O, different regions including reaction, transition and diffusion zones were identified in both samples. The glass samples with higher amounts of Al content have a significantly narrower reaction zone than the low Al materials.

Thin Films
Room 203 - Session TF-TuA
Mechanical Properties of Thin Films

Moderator: B. Starks, Veeco-CVC

2:00pm **TF-TuA1 The Nanomechanical Properties of Thin Films***,* ***J.E. Houston,*** Sandia National Laboratories. **INVITED**

Material properties and processes can appear remarkably different when viewed at the nanometer level. Mechanically, solids can approach the behavior of perfect single-crystals and inter-particle interactions become dominated by surface energetics and dyna mics. In thin films with nanometer scale grains, dislocation-loop formation can become unfavorable and grain sliding can become the dominant mechanism for plastic deformation. The study of the mechanical properties of these materials is presently enjoying increasing attention due in large part to the rapid development of scanning-probe techniques capable of making measurements on individual grains down to the nanometer level. In this presentation, I will illustrate some of these unique nanoscale effects in various applications of the Interfacial Force Microscope (IFM) to studies of the nanomechanical properties of thin films. The IFM is a scanning force-probe microscopy similar to the Atomic Force Microscope but distinguished by its use of a mechanically stable, zero compliance force sensor. Used in a nanoindenter mode, this sensor offers accurate control of the probe-sample separation and provides a quantitative measure of the film's mechanical behavior. I will illustrate the IFM's unique capabilities w i th examples of near theoretical yield strength for single-crystal surfaces and the effect of surface steps on the strength. In polycrystalline films, I contrast the mechanical behavior as a function of grain size and film thickness and discuss the mechanisms responsible for the interesting observations. 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.

2:40pm **TF-TuA3 Anomalous Plastic and Elastic Behaviors of Sputter-deposited TiN with 10 or 20 Inserted Thin Al Layers Evaluated by Nanoindentation***, **E. Kusano**, N. Kikuchi, K. Tsuda, H. Nanto, A. Kinbara,* Kanazawa Institute of Technology, Japan

The hardness enhancement observed for multilayered thin films results from the specialized mechanical properties of the interface region. In this paper, effects of thin Al layers inserted into the TiN matrix thin film on mechanical properties of the coating have been investigated in order to discuss a role of the interface regions made by the Al thin layer insertion. Thin films of TiN with Al thin layers have been deposited by dc magnetron sputtering. The total TiN thickness was kept at 500 nm for all prepared samples. The number of thin Al layers inserted was varied from 2 to 20 for the total Al thickness of 100 to 500 nm. The top layer of the coating was TiN for all sample coatings. Film hardness of prepared samples was estimated by nanoindentation. From a load-unload curve of the nanoindentation, energies consumed to induce plastic deformation and elastic deformation were estimated. A hardness of thin films with 20 Al layers decreased from 11 GPa to 8GPa when the total Al layer thickness increased from 100 to 500 nm. For a constant total Al layer thickness, the film with 20 Al layers yielded higher hardnesses. The film with 20 Al layers with a layer thickness of 5 nm was harder than the monolithic TiN film. While the energy used for plastic deformation during nanoindentation increased with the total Al layer thickness, the energy used for elastic deformation remained constant. Further, the dissipated energy decreased with increasing the number of Al layers inserted. These results obtained by nanoindentation measurement imply that the film becomes more elastic with increasing the number of Al layers inserted. A high microhardness obtained for a film with Al layer thickness of 5nm emphasizes a unique effect of thin Al layers or interface regions on mechanical properties of the coating.

3:00pm **TF-TuA4 Tungsten Silicide (WSi2) for the Alternate Gate Metal in Metal-Oxide-Semiconductor (MOS) Devices***, **K. Roh**, S. Youn, S. Yang, Y. Roh,* Sungkyunkwan University, Korea

Recently, it has been recognized that both achieving low gate resistance and suppressing poly-Si gate depletion are key factors for developing deep submicron MOSFETs. In the present work, tungsten silicide (WSi2) deposited directly on SiO2 is proposed for the alternate gate electrode for deep-submicron MOSFETs. PMOS capacitors were fabricated on 4~7@ohm@-cm, (100) n-type Si wafers. Thermal oxidation of the Si was carried out at 850°C for 80 s using RTP to grow ~110Å SiO2. WSi2 were then deposited directly on SiO2 in a cold-wall LPCVD system: Deposition temperature and pressure were 350°C and 0.7Torr, respectively. The ratio of SiH4/WF6 flow was changed from 40 to 70. RTP was used for post-deposition annealing at various conditions. Detailed analysis of mechanical properties of WSi2 deposited on SiO2 reveals that a low resistivity can be obtained while satisfying the requirement for the low thermal budget. In addition, HTEM results showed that WSi2-SiO2 interface remains very flat after annealing as-deposited WSi2 films using RTP at 780°C in vacuum. Since F diffusion into SiO2 during the WSi2 deposition and annealing steps has been known to cause the irregular formation of WSi2-SiO2 interface, we attribute the current results to the indirect evidence of negligible F diffusion. In addition, the electrical characteristics of annealed WSi2-SiO2-Si (MOS) capacitors were also improved in view of charge trapping. For example, oxide charging curves monitorted during Fowler-Nordheim tunnel electron injection indicate that the shift of flatband voltage is less for RTP annealed samples as compared to that of as-deposited samples. The phenomenon of gate depletion which has been a serious problem of poly-Si gate is also suppressed in the WSi2 gated MOS capacitors. The C-V data shifted to the positive gate bias after annealing, and we interpret that this positive shift is caused by the workfunction difference that may be caused by the change of Si to W ratio due to the annealing process.

3:20pm **TF-TuA5 Structural and Mechanical Properties of TiC/Ti and TiC/B@sub 4@C Multilayers Deposited by Pulsed Laser Deposition***, **A.R. Phani**, J.E. Krzanowski,* University of New Hampshire*; J.J. Nainaparampil,* Systran, Inc.

Multilayer thin films have been shown to enhance the hardness as well as toughness of hard ceramic coatings, and the results often depend on the type of interlayer used. In the present study, we have investigated multilayers of TiC/Ti (for toughness enhancement) and TiC/B@sub 4@C (for hardness enhancement). Films were deposited on 440C steel and silicon substrates by pulsed laser deposition (PLD). Ti, B@sub 4@C and TiC targets were ablated in a background gas of 1mTorr Ar at substrate temperatures of 200, 400 and 600C. Samples were deposited having modulation periods ranging from 2.5 to 50 nm. Films were analyzed using nano-indentation hardness, x-ray diffraction, XPS and electron microscopy. Surface morphology and roughness of the samples were measured by scanning electron microscopy and atomic force microscopy, respectively. Tribological studies have also been conducted to evaluate the friction and wear properties of these films. Films with low modulation periods showed lower residual stresses as measured by x-ray diffraction methods. The nano-indentation hardness of compositionally modulated Ti/TiC and TiC/B@sub 4@C multilayer films were found to be dependent on composition modulation frequency. TiC/Ti films showed reasonably high hardness values (37GPa) for the lower period samples despite the incorporation of the metal layer, and TiC/B@sub 4@C films showed hardness levels up to 42GPa. Film composition depth profiles performed by using XPS showed 1-2 at % oxygen in the deposited films, as well confirming the presence of composition modulations. The mechanisms of hardness enhancement and its relation to tribological properties will also be discussed.

3:40pm **TF-TuA6 Structural Studies of AlN Thin Films during Low Temperature RF Sputter Deposition***, **F. Engelmark**, G.F. Iriarte, I.V. Katardjiev, M. Ottosson,* University of Uppsala, Sweden*; P. Muralt,* Laboratiore de Ceramique, Switzerland*; S. Berg,* University of Uppsala, Sweden

AlN is a material used in a wide variety of applications such as electro-acoustic devices, blue diodes, IR-windows, thermal conductors, MIS-structures, IC-packaging, etc. Thin piezoelectric AlN polycrystalline films have been grown on Si and SiO@sub 2@ using RF magnetron sputter deposition in an Ar/N@sub 2@ gas mixture. The structural properties of the films have been optimized by varying the deposition parameters, such as process pressure, gas mixture, substrate temperature, discharge power, etc. It was found that the best film texture was obtained for a particular set of parameters, namely process pressure of 8 mTorr, substrate temperature 350°C, discharge power 350W and a gas mixture of 25%Ar and 75%N@sub 2@. The films as examined by XRD exhibited a columnar structure with a strong (002) texture, and a FWHM rocking curve of 1.6 degrees. A crystallite size of 38 nm was calculated using Sherrers formula. AFM measurements indicated a surface roughness with an rms value of 8 Å. Classical nonapodized transversal SAW filters operating at a frequency of 534 MHz were fabricated to estimate the electro-acoustic properties of the films. The measurements indicated a coupling coefficient of 0.46% and a phase velocity of 4900 m/s. Further, thin epitaxial films were grown on alfa-Al@sub 2@O@sub 3@(001) under the same deposition conditions. The films exhibited a (001)AlN//(001)alfa-Al@sub 2@O@sub 3@ plane orientation with a (002) rocking curve FWHM value of about 0.4 degrees, indicating a relatively good alignment of the c-axis or a low dislocation density. The in-plane orientation was [110]AlN//[120]alfa-Al@sub 2@O@sub 3@ corresponding to a rotation of the AlN film of 30 degrees with respect to the alfa-Al@sub 2@O@sub 3@(001) surface. Cross-sectional TEM studies indicated a population of both thread and edge dislocations with decreasing concentrations with film thickness.

4:00pm **TF-TuA7 Multifunctional Ceramic Films***, **C.R. Aita**,* University of Wisconsin, Milwaukee **INVITED**

The concept of a film that can perform different functions as required by changing external stimuli has long intrigued scientists and engineers. The nanostructure revolution has made possible new uses for ceramic films that behave as multifunctional "smart" materials. In this paper, we first review new developments in traditional uses for multifunctional films, such as those involving electrochromic and thermochromic materials. Next, we describe new uses for multifunctional ceramic films. The design and development of a biocompatible coating that protects blood-interfacing implants against corrosion and mechanical degradation is used as an example of the challenges that face synthesis and characterization of these multifuctional "smart" materials.

4:40pm **TF-TuA9 Quantification of Scratch Resistance and Accelerated Wear for Thin Film Coatings Using the Newly Developed Micro-Tribometer and Testing Procedure***, **C. Gao**, N. Gitis,* Center for Tribology

Quantification of scratch and accelerated wear resistance of thin films ranging from 1 nm to 1000 nm was achieved by using critical loads, at which the given films were progressively worn through. Progressive worn through of thin carbon films (3 nm to 8 nm) on magnetic disks using a micro-blade under precision motion with linearly increasing loads from 0.2 grams up to 400 grams was clearly observed simultaneously from electrical contact resistance (ECR), friction force and acoustic emission (AE) signals. At the critical load, friction force and AE fluctuated violently and ECR dropped to practically zero. The critical load was found to increase with increasing carbon thickness, as expected. The wear depths at the critical loads were measured post-test using Tencor profiler and optical surface reflection and found to be in excellent agreement with film thickness. A lubricant film as thin as 1 nm on the carbon films enhanced the critical load by a factor of five to ten. The same testing procedure was applied for thicker diamond-like carbon films on silicon substrate ranging from 50 nm up to 1000 nm, but with linearly increasing loading force from 0.2 N up to 40 N. Good correlation was found between critical load and film thickness, and also between critical load and residue film stress also. However, there was no correlation between critical load and nano-hardness. We believe that the nanohardness measurements may not apply for films thinner the sub-micrometer, since the contact stress distributed well into the substrate when nano indentation was made. The successful quantification of scratch resistance and accelerated wear is attributed to precision motion, linearly increasing load mechanism and the contact geometry of the micro-blade. The micro-blade will be described and the mechanism for its effectiveness on surface film evaluations will be discussed, as compared to much less effective counter surfaces, such as a diamond stylus or a stainless steel ball.

5:00pm **TF-TuA10 Lubricating Characteristics of Zinc Oxide: Effect of Carbon, Silicon and Boron as Additives***, **J.J. Nainaparampil**,* Systran Federal/Air Force Research Lab*; J.S. Zabinski,* Air Force Research Lab

Zinc Oxide, with its wurzite structure, is a unique material that exhibits lubricious qualities and desirable electronic and optical characteristics. There have been numerous studies on the doped zinc oxide thin films profiling it as an optical coating material or as a semiconductor material. But no significant amount of work has been reported yet on this material as a tribological material. Recent work of this lab revealed some of the tribological potentials of this material. Due to its open nature and desirable coordination number, zinc can move around different lattice positions and be substituted with external atoms to become interstitials. Zinc oxide shares the hexagonal structure, which is commonly seen in most of the widely used solid lubricants. The open nature of its crystal structure and similarity of this structure with that of the widely used solid lubricants are quite desirable qualities. To preserve these qualities, and to manipulate the tribological characteristics, additives of ionic radii comparable that of Zn need to be selected. Alumina doped zinc oxide have already been studied and found to have low friction and good wear characteristics. In this work, properties of thin films of zinc oxide, formed with simultaneous addition of Si, C and B will be reported. Si added films showed low friction and long wear life above 350 ÂºC. Deposition direction and oxygen working pressure also had a profound effect on these films. Results of common surface analyzing techniques like XPS, SEM, AFM, and XRD, Raman, Nanoindentation and Friction and Wear will be reported.

Electronics
Room Exhibit Hall C & D - Session EL-TuP
Poster Session

EL-TuP1 Polarization Effect on Copper Electroplating in Presence of Thiourea Additives*, **C.-L. Cheng**, Y.-S. Lin,* Chung-Yuan University, Taiwan

Copper metallization will play an important role in future microelectronic processing because Cu has lower resistivity and higher electromigration resistance compared to Al. Copper could be deposited by either physical sputtering, chemical vapor deposition (CVD), or electrochemical deposition. Since electroplating has advantages of low processing temperature, short processing time, and simple deposition facilities, which compared to traditional sputtering and CVD, electroplating becomes the most attractive techniques implemented in Cu metallization. Polarization becomes very important in Cu electroplating because it could effect formation of copper grain and copper filling mechanism. One common method to change the degree of polarization is using chemical additives during electroplating. In order to realize polarization effect on copper formation during electroplating, we choose a series of thiourea additives: thiourea, N-acetylthiourea, and N,N-diethylthiourea used as chemical additives on copper electroplating. Since N,N-diethylthiourea has a pair of electron-pushing groups (di-ethyl groups), it could enhance electron density around sulfur atom to increase interaction with copper ions and make polarization higher. The results are shown polarization will become higher when N,N-diethylthiourea is present and lower when N-acetylthiourea (electron puller) is existed. The finer grain size of copper forms when the higher polarization appears. Based on this study, we demonstrate that N,N-diethylthiourea could be used to act as gap filling promoters without void formation in the 0.25 micrometer dimension of trench with an aspect ratio of 4.

EL-TuP2 Low Temperature, Single-Source CVD of ZrB2 and HfB2 Films as Cu Diffusion Barriers and Interconnects in Next-Generation ULSI*, **J.H. Sung**, D.M. Goedde, G.S. Girolami, J.R. Abelson,* University of Illinois at Urbana-Champaign

Thin films of the metallic ceramics ZrB@sub 2@ and HfB@sub 2@ have high electrical conductivity and are very effective diffusion barriers against copper; hence, they are attractive as interconnect and barrier materials for next-generation ULSI technology. Previously, we deposited highly conformal (~ 100 % bottom coverage) ZrB@sub 2@ and HfB@sub 2@ films using Zr(BH@sub 4@)@sub 4@ and Hf(BH@sub 4@)@sub 4@ single-source precursors in a CVD reactor with a remote hydrogen plasma source. The atomic H enhanced the release of excess B from the growth surface at low temperature, producing stoichiometric films with excellent properties. The film structure could be controllably varied from amorphous to polycrystalline by varying the substrate temperature from 250 - 800 °C, while maintaining stoichimetry. Here, we demonstrate that a single layer of ZrB@sub 2@ or HfB@sub 2@ can successfully replace the complex W/TiN/TiSi@sub 2@ multilayer that is currently used for ULSI metallization of Si. To achieve low contact resistivity on p-type Si, we adjust the ZrB@sub 2@ or HfB@sub 2@ stoichiometry during the initial deposition in order to provide a controlled source of excess B atoms. This is done by briefly reducing the remote hydrogen plasma power, which increases the B content above stoichiometric ratio. We will also present results for ZrB@sub 2@ or HfB@sub 2@ deposited at < 300 °C: electrical resistivity less than 40 µm@ohm@-cm, effective diffusion barrier against Cu during annealing to 700 °C for 1 hour, and low specific contact resistivity.

EL-TuP3 Study of Electrical and Interfacial Properties of CVD-W/n-Si@sub 0.83@Ge@sub 0.17@/Si(001) Schottky Contacts*, **Y.C. Jang**, K.S. Kim, D.O. Shin,* Sungkyunkwan University, South Korea*; K.-H. Shim,* Electronics and Telecommunications Research Institute, South Korea*; S. Youn, K. Roh, Y. Roh, N.-E. Lee,* Sungkyunkwan University, South Korea, Korea

The formation of metal contacts on Si@sub 1-x@Ge@sub x@ alloys plays an essential role in the various devices utilizing Si@sub 1-x@Ge@sub x@/Si including heterojunction bipolar transistors, and photodetectors. Therefore, interactions between the metals and the Si@sub 1-x@Ge@sub x@ layers are of technical and scientific interests for understanding of Schottky barrier formation. Chemical vapor deposited W as a refractory metal has been commonly used in microelectronics industry and has several characteristics that make it very attractive candidates for contact metallization. The effective Schottky barrier height measurements on the CVD-W/n-Si@sub 1-x@Ge@sub x@(001) system, however, have not reported so far as we know. In this study, we investigated the electrical properties of CVD-W/n-Si@sub 1-x@Ge@sub x@(x=0.17) and CVD-W/n-Si schottky contacts. Fully-strained 90-nm-thick n-type Si@sub 0.83@Ge@sub 0.17@ epitaxial thin film with the P concentration of 5x10@super 17@ cm@super -3@ was deposited on p-type Si(001) substrate at the substrate temperature of 650°C by LPCVD utilizing SiH@sub 4@, GeH@sub 4@, PH@sub 3@, and H@sub 2@ gases. W layers were grown by LPCVD using the WF@sub 6@, SiH@sub 4@, and H@sub 2@ at the growth temperature of 350 - 550°C. W Schottky contacts with various sizes from 0.2 mm@super 2@ to 0.5 mm@super 2@ were defined by photolithography and etching. Electrical properties of the CVD-W/n-Si@sub 0.83@Ge@sub 0.17@ Schottky diodes were characterized by I-V measurements in the forward-biased direction at room temperature. The measured effective Schottky barriers (@PHI@@sub Bn@) for CVD-W/n-Si@sub 0.83@Ge@sub 0.17@ and CVD-W/n-Si were 0.553 eV and 0.671 eV at the W deposition temperature (450°C).The structural, chemical and interfacial properties of CVD-W/n-Si@sub 1-x@Ge@sub x@(x=0.17) interfaces were analyzed by XRD, TEM, RBS, and AES. The correlation between electrical and structural properties of their interfaces will be discussed.

EL-TuP4 Work Function and Barrier Height Correlation for Al/GaAs Schottky Contacts Modified by Ultra-Thin, Doped Si and Ge Interlayers*, **T.A.R. Müller**, M.I. Nathan,* University of Minnesota*; A. Franciosi,* University of Minnesota and Universita' di Trieste*; C.J. Palmstrom,* University of Minnesota

A promising alternative to alloyed contacts to GaAs, which suffer from lateral diffusion and spiking problems, is the deposition of ultra-thin (1eV, while the co-deposition of Si with As shows an increase in the work function of 0.2eV for a Si-coverage of 0.5ML. The corresponding barrier height lies in the 0.2eV range. In this talk, we report a systematic study of the effect of Ge interlayers (

EL-TuP5 Enhancement of Mobility with Double Delta-doped Quantum Wires by Focused Ion Beam*, S. Choi, M. Leung, G. Stupian, N. Presser,* The Aerospace Corporation*; **C. Lee**,* Honam University, Korea

100nm wide delta-doped quantum wires were fabricated by the Molecular Beam Epitaxy (MBE) and a subsequent Focused Ion Beam (FIB) milling process. Ion beam focused to submicrometer diameters offers a radical departure from the conventional fabrication routine for quantum wires such as electron beam lithography. First of all,all the double delta-doped AlGaAs/GaAs quantum well structures were grown by solid source MBE system. N-type delta-doping was made in the spacer region close to the well during the MBE growth. The structures grown are a single well with two 100nm AlGaAs spacers. 5 micrometer wide Hall bar mesas were prepared by the optical lithography and a subsequent chemical etching. Next, 100nm wide AlGaAs/GaAs quantum wires were made by a 25KeV focused Gallium ion beam at 10pA current. The excited subbands in the quantum well structures may have significant amount of carrier densities placed in the undoped region where Coulombic scattering is reduced. In addition to the delta-doping effect on the reduction of scattering, one dimensional confinement effect due to 100nm wide wire structures may contribute to the enhancement of mobility along the wire direction. As a result, three times enhancement of mobility compared to the quantum well structures were found in the low temperature Hall measurements with double delta-doped quantum wires. This type of structures and a fabrication technique may show great promise for obtaining high mobility with high densities for semiconductor devices.

EL-TuP6 Implantation of AlAs Etch-Stop Layers by MBE for Recessed Gate P-HEMTs*, G. Zhou, W. Liu, **M. Lin**,* Alpha Industries, Inc.

The AlGaAs/InGaAs/GaAs pseudomorphic high electron mobility transistor (p-HEMT) has been widely accepted for many high-performance, low cost millimeter-wave applications and high-speed digital circuits. In HEMTs fabrication process, one of the most critical steps is gate recess etching. This is because recess groove profiles have significant influences on the DC and RF performance of devices and integrated circuits as a whole. Wet-chemical etching is a conventional but important approach to conducting recess etching due to its ease of use and its capability to tailor device performance. To precisely control the gate recess process, the implantation of an etch-stop layer into the p-HEMT device structure is highly desirable. AlAs is a traditional etch-stop material to GaAs because of its high etching selectivity (~ 400x) and near perfect lattice match. For a reliable and controllable etching process, a reasonable thick etch-stop is desired. However, due to its large bandgap (~2.2eV) and higher defect density (DX center, for example), thick AlAs layer may cause ohmic contact problem and other side-effects which would degrade the device performance. We report the study of MBE growth of AlGaAs/InGaAs pHEMT structure with double AlAs etch-stop layers. The thickness of the AlAs etch-stoppers ranging from 1.0 to 2.5 nm. The structures were studied by Hall measurement, high-resolution x-ray diffraction, photoluminescence (PL) and photoreflectance (PR). The selective etching behavior was verified by etching profiles of time dependent sheet charge density from Hall measurements. The correlation between the etching selectivity and ohmic contact resistivity, as well as the device performance of the p-HEMT structure was compared for different structures to get the optimum AlAs thickness.

EL-TuP7 Early Growth Studies of Barium Magnesium Fluoride onto (111)-oriented Silicon Substrates*, A. Martinez, **W. Gomez**, M. Rodriguez,* University of Puerto Rico

We have grown barium magnesium fluoride films (BMF) onto (111)-oriented silicon substrates using molecular beam epitaxy. The early stages of growth were studied through the performance of X-ray photoelectron spectroscopy measurements on interrupted growth runs without exposing films to atmosphere. It was observed that exposure of the Si substrate to the BMF vapor at a substrate temperature of 950C for periods of 10 seconds, removed the native oxide layer from the substrate. Subsequent growth onto substrates pretreated in this way resulted in highly textured (020)-oriented BMF films, as evidenced by x-ray diffraction studies. Films grown without the pretreatment did not display this high degree of texture.

EL-TuP8 Fabrication of Smooth Diamond Films on SiO2 by the Addition of Nitrogen to the Gas Feed in Hot-filament CVD*, V. Baranauskas, A.C. Peterlevitz, Z. Jingguo, **S.F. Durrant**,* Universidade Estadual de Campinas, Brazil

Diamond films of low roughness have been deposited onto thermally oxidized Si substrates by a process of anisotropic crystalline growth induced by nitrogen in a Hot-Filament Chemical Vapor Deposition (HFCVD) reactor. Ethanol (C2H5OH), diluted in hydrogen and nitrogen, was used as the source of carbon. At high concentrations, nitrogen tends to suppress diamond growth in the < 100 > direction, which allows the growth of square mesoscopic crystals of great area in the directions parallel to the surface of the substrate. These mesoscopic structures of low thickness stack upon each other, forming a thick diamond coating of uniform thickness. Analysis of the coatings made by micro-Raman spectroscopy and atomic force microscopy (AFM) revealed that it is possible to obtain diamond coatings of high quality of roughness comparable that of the SiO2 at the diamond/SiO2 interface, and the roughness at the growth surface corresponds to the thickness of the steps of the mesoscopic structures. The microscopic mechanisms that involve the possible passivation of the diamond surface by nitrogen are also discussed.

EL-TuP9 Nanocrystalline Diamond and Nano-carbon Structures Produced using a High Argon Concentration in Hot-filament CVD*, V. Baranauskas, **A.C. Peterlevitz**, H.J. Ceragioli, S.F. Durrant,* Universidade Estadual de Campinas, Brazil

Nanocrystalline diamond and nano-carbon structures in the form of wires have been grown by the introduction of argon at high concentrations (60 % to ~ 99.5 % vol. Ar) into the feed mixture (ethanol and hydrogen) of a hot-filament CVD reactor. Besides the chemical inertness of argon, its presence in the gas phase changes the kinetics of the carbon deposition process. The addition of argon induces an increase in the density of vacancy defects in the diamond structure, increases the flaws between the grains, the porosity of the films, and forms new carbon structures. The range of concentration of argon used in this work is very interesting since it covers the phase transition between porous diamond (~60 % vol. Ar) and carbon nanowires (~ 99.5 % vol. Ar). A critical discussion of the growth kinetics and morphological data obtained by scanning electron microscopy (SEM), micro-photoluminescence and micro-Raman spectroscopy are discussed.

EL-TuP10 Bonding Chemistry of Alternative Gate Dielectrics: Is there Really an Alternative Gate Dielectric that can Meet SIA Roadmap Expectations for Performance, Reliability and Process Integration?*, **G. Lucovsky**,* North Carolina State University

This paper presents a new classification scheme for non-crystalline metal oxides that have been considered as replacements for SiO@sub2@ in Si devices with channel lengths < 100 nm.. The scheme is based on relative bond ionicity, and the scaling parameter is the difference in the Pauling electronegativity, @Delta@X, between the oxygen, X(O), and metal (semiconductor), X(M), atoms. This approach distinguishes between three groups of non-crystalline elemental oxides with different bonding micro-structures: i) @Delta@X < 1.6 - covalent random networks such as SiO@sub2@, B@sub2@O@sub3@, and P@sub2@O@sub5@, ii) 1.6< @Delta@X < 2.0 - random amphoteric networks with interstitial ions such as Al@sub2@O@sub3@ and Ta@sub2@O@sub5@, and iii) @Delta@X > 2 - random close packed ionic structures such as Zr(Hf)O@sub2@, and Y(La)@sub2@O@sub3@. This approach has been extended to binary oxides and alloys. Systematic trends in atomic bonding arrangements and thermal stability with increasing @Delta@X are addressed for i) elemental oxides such as Al@sub2@O@sub3@, Ta@sub2@O@sub5@ and ZrO@sub2@, and ii) binary silicate alloys, such as (ZrO@sub2@)@subx@(SiO@sub2@)@sub(1-x)@ that span the entire range of @Delta@X. As @Delta@X increases, the atomic coordination of the metal atom increases, and thermal stability with respect to crystallization decreases. Three factors limit application of alternative oxides/silicates with @Delta@ X> 1.6 as gate dielectrics in Si devices. These are i) reactions with Si substrates, and/or intentionally-grown thin SiO@sub2@ interfacial layers that occur during film deposition and/or annealing, ii) thermal stability against chemical phase separation and/or crystallization which limits post-deposition processing temperatures, and iii) an inherent ion polarization contribution to the frequency dependent conductance that can degrade high frequency electrical performance.

EL-TuP11 Electrical Properties of (Ba,Sr)TiO@sub 3@ Capacitors by Inductively Coupled Plasma Etching*, **S.-K. Choi**, N.-H. Kim, E.-G. Chang,* Chungang University, Korea*; T.-H. Kim,* YIT, Korea*; C.-I. Kim,* Chungang University, Korea

Recently, (Ba,Sr)TiO@sub 3@ high dielectric thin films have received much attention as a new dielectric material for high density dynamic random access memories (DRAMs) because of their high relative dielectric constant and small variation in dielectric properties with frequency. It is well known that BST films are difficult to be etched, but good etch rate with high selectivity to etch mask was obtained by result of our former study.@footnote 1@ However, It was scarcely verified the possibility of etched thin films under these conditions for the appliance of practical devices. In this study, high density plasmas etching damage to the electrical properties of Pt/(Ba,Sr)TiO@sub 3@/Pt high dielectric capacitors was evaluated under Ar bombardment and Ar/Cl@sub 2@/BCl@sub 3@ etch plasmas. And the etch parameters were changed as gas mixing ratio, coil rf power, dc bias voltage and chamber pressure. Capacitance and leakage current of BST capacitors, before and after etching, are compared to examine the etching damage. The capacitance and dielectric dissipation factors were measured by using an HP 4192 impedance/gain-phase analyzer at 10 kHz, and the leakage current density was determined by using an HP 4145B semiconductor parameter analyzer. The change of capacitance and leakage current represented the physical effect of ion bombardment. The crystal structure of the etched samples was investigated by x-ray diffraction (XRD) to observe the variation of phases. The improved etching condition with the consideration of capacitance and leakage current of BST capacitor could be obtained by analyzing correlation between electrical properties and various etching parameters. . @FootnoteText@ @footnote 1@ S.-B. Kim, Y.-H. Lee, T.-H. Kim, G.-Y. Yeom, and C.-I. Kim, J. Vac. Sci. Technol. A 18, 2000. To be published.

EL-TuP12 (1-x)SrTiO@sub 3@-xPbTiO@sub 3@ Thin Films Grown by RF Sputtering on Pt/TiN@sub X@ AND RuO/TiN@sub X@ Electrodes*, **E.M. Guerra**,* CICESE, Mexico*; A.F. Cruz,* IMRE, Mexico*; J.S. Beltrones,* UNAM, Mexico

(1-x)SrTiO@sub3@(ST)-xPbTiO@sub 3@(PT)polycrystalline thin films were deposited at different temperatures and pressures by argon ion rf sputtering on Pt/TiN@sub x@/SiO@sub 2@/Si and RuO/TiN@sub x@/SiO@sub 2@/Si substrates in presence of different concentration of Oxygen. The polycrystalline (ST-PT) perovskite phase formation is confirmed by x-ray diffraction (XRD) analysis and the grain growth dynamics is studied by scanning electron microscopy (SEM). The nature of the ferroelectric layer-electrode interface is analyzed by transmission electron microscopy (TEM) as well as the effect of its characteristics in the performance of the multilayer system. The dielectric properties of the ST-PT thin films were characterized through P-E hysteresis measurements. The microstructural results obtained for the (1-x)SrTiO@sub 3@-xPbTiO@sub 3@ films on Pt/TiN@sub x@/SiO@sub 2@/Si and RuO/TiN@sub x@/SiO@sub 2@/Si substrates were correlated to the ferroelectric properties.

EL-TuP13 Etching Mechanism of Y@sub 2@O@sub 3@ Thin Flims in Cl@sub 2@/Ar Plasma*, **Y.C. Kim**, B.J. Min,* Chungang University, Korea*; Y.T. Kim,* KIST, Korea*; C.-I. Kim,* Chungang University, Korea

Many researchers have proposed to insert such buffer layers as Y@sub 2@O@sub 3@ and CeO@sub 2@ for ferroelectric gate structures. In particular, Y@sub 2@O@sub 3@/Si shows excellent interface properties and ferroelectrics deposited on Y@sub 2@O@sub 3@ film show excellent fatigue characteristics. The dielectric constant of Y@sub 2@O@sub 3@ film ranges from 14 to 17. Hence, Y@sub 2@O@sub 3@ films are expected to be used a buffer layer in the ferroelectric gate structure. In this study, etching mechanism of Y@sub 2@O@sub 3@ thin film was systematically investigated by using inductively coupled Cl@sub 2@/Ar plasma. Etching characteristics of the Y@sub 2@O@sub 3@ thin film were investigated by using plasma diagnostic tools in conjunction with the surface analysis after etching. The etch rate of Y@sub 2@O@sub 3@ film, and selectivity of Y@sub 2@O@sub 3@ film to PR and SiO@sub 2@ were examined as functions of Cl@sub 2@/Ar gas mixing ratio, coil rf-power, dc bias voltage, chamber pressure, and substrate temperature. The etched surface of Y@sub 2@O@sub 3@ film was examined with x-ray photoelectron spectroscopy (XPS) and secondary ion mass spectrometry (SIMS). The etch profile of Y@sub 2@O@sub 3@ film was examined with scanning electron microscopy (SEM). The concentrations of the etching species in the plasma were determined by using optical emission spectroscopy (OES). Plasma potential and floating potential, electron density and ion current density in the plasma were determined by using Langmuir probe. Y@sub 2@O@sub 3@ film was more effectively etched by Ar ion bombardment than by chemical reaction with Cl radical, but the etch rate of Y@sub 2@O@sub 3@ film was enhanced by chemical reaction with Cl radical. In this study, for the first time, we introduced the use of Cl@sub 2@/Ar plasma system in Y@sub 2@O@sub 3@ etching.

EL-TuP14 Etch Characteristics of CeO@sub 2@ Thin Films as a Buffer Layer for the Applications of MFIS-FeRAM*, C.-S. Oh,* Chungang University, Korea*; K.-H. Kwon,* Hanseo University, Korea*; T.-H. Kim,* YIT, Korea*; C.-I. Kim,* Chungang University, Korea

Cerium oxide (CeO@sub 2@) thin film has been proposed as a buffer layer between the ferroelectric film and the Si substrate in Metal-Ferroelectric-Insulator-Silicon (MFIS) structures for ferroelectric random access memory (FeRAM). CeO@sub 2@ thin film has properties of high thermal stability, high dielectric constant and good lattice match with Si. Since the etching of CeO@sub 2@ thin film has not been reported, we studied the etch characteristics of CeO@sub 2@ thin films by using high density plasma etching system. In this study, CeO@sub 2@ thin films were etched with a CF@sub 4@/Ar gas combination in an inductively coupled plasma (ICP). Mask made use of photoresist (PR). The experiment was done by controlling the etching parameters such as gas mixing ratio, radio frequency power, direct current bias, and chamber pressure. The surface reaction of the etched CeO@sub 2@ thin films was investigated with x-ray photoelectron spectroscopy (XPS) using narrow scan spectra. Ar ion bombardment is more dominant than chemical reaction between Ce and F. The results of XPS analysis were verified by results of secondary ion mass spectrometer (SIMS) analysis and results were the same. In addition, Optical emission spectroscopy (OES) was investigated to analyze density of F radical and Ar ion in plasma. Ion current density was measured by using single Langmuir probe. The etch products were also determined using a quadrupole mass spectrometer (QMS). The profile of etched CeO@sub 2@ thin film investigated with scanning electron microscopy (SEM).

EL-TuP15 The Interface Formation of Ta and Low-k Plasma-polymerized Para-xylene (PPpX) and Cyclohexane (PPCHex) and the Diffusion Properties*, K.J. Kim,* *K.S. Kim, Y.C. Jang,* Sungkyunkwan University, South Korea*; G.Y. Yeom, N.-E. Lee,* Sungkyunkwan University, South Korea, Korea*; Y.C. Quan, J. Choi, C.Y. Park,* Sungkyunkwan University, South Korea*; D.-Y. Jung,* Sungkyunkwan University, South Korea, Korea

In order to decrease the RC delay of integrated circuit, there have been extensive research activities on Cu interconnect technology utilizing low dielectric constant (low-k) interlayer dielectric materials and Cu to replace the conventional Al metallization scheme. One of the candidates for low-k dielectrics is the organic thin films prepared by various methods. Particularly, low-k plasma-polymerized organic films containing no F which causes various corrosion problems are very promising. However, they do not provide a good interfacial adhesion to metals due to the absence of bonding states between metals and plasma-polymerized low-k organic films. In this study, we investigated the interface formation and diffusion properties between Ta and low-k plasma-polymerized para-xylene (PPpX) and cyclohexane (PPCHex) thin films as a function of O@sub 2@ or N@sub 2@ plasma-treatment conditions using XPS and RBS. Low-k plasma-polymerized thin films were prepared on silicon substrates by PECVD using the para-xylene and cyclohexane precursors at the substrate temperature of 45°C. PPpX and PPCHex were shown to have the dielectric constant as low as 2.70 and thermal stability up to 450°C. Plasma-treatments were performed by MEICP at the inductive power of 400W by keeping the O@sub 2@ and N@sub 2@ flow at 10sccm, respectively. Ta with the film thickness of 40Å was deposited using an electron-beam evaporator at room temperature. These samples were annealed at 450 ~ 500°C in vacuum in order to investigate the interface formation and diffusion of Ta into low-k films. We found that the Ta-C, due to newly created additional functional group, was formed between Ta layer and plasma-treated low-k films, judged from XPS measurements. The diffusion of Ta into the PPpX and PPHex was negligible in the detection limit of RBS.

EL-TuP16 Structure Effects of Pendant Groups on Dielectric Constant and Thermal Properties of Polyimides*, L.-Y. Wang,* National Taiwan University, Taiwan*; P. Chang, C.-L. Cheng,* Chung-Yuan University, Taiwan

Polyimides exhibit high thermal and mechanical properties, are easily processable as thin films from soluble precursors, and have desirable dielectric properties. In this study, we investigate the structure-property on a series of polyimides which contain alkyl side groups. Two series of high molecular weight polyimides have been synthesized by the reaction of benzophenonetetracarboxylic dianhydride (BTDA) or hexafluoroisopropylidene bis(phthalic anhydride) (6FDA) with 4,4'-methylenedianiline (MDA), 4,4'-methylene-bis-(2,6-dimethylaniline) (MBDMA), 4,4'-methylene-bis-(2,6-diethylaniline) (MBDEA) or 4,4'-methylene-bis-(2,6-diisopropylaniline) (MBDIA). The introduction of fluorine into polyimides may vary free volume and polarizability and effect dielectric constant and thermal properties. The introduction of different side groups may change free volume and effect dielectric property. In this research, a detailed structure effect on the dielectric constant and thermal properties of polyimides containing alkyl side groups will be illustrated.

Flat Panel Displays
Room Exhibit Hall C & D - Session FP-TuP
Poster Session

FP-TuP1 Fabrication and Characterization of Blue Light Emission from a Well-Type Field Emitter Device Implementing a Thin Film ZnO:W Phosphor*, V. Bhatia,* *H.R. Kim, M.H. Weichold,* Texas A&M University

Flat panel displays based on the principals of field emission, in theory, can delivery a picture quality comparable to a cathode ray tube at lower voltages with efficient phosphors. Microtip fabrication and availability of low voltage blue light emitting phosphors have been some of the key issues of research for the commercialization of these displays. This paper presents the fabrication of lateral edges as electron sites to produce blue light from the co-deposited thin film of zinc oxide and tungsten. The phosphor used in the lateral edge field emitter device has been fabricated at Texas A&M University@footnote 1@ by co-depositing zinc oxide and tungsten and annealing the thin film under appropriate annealing conditions. Phosphor emits blue light (490nm) at voltages as low as 300 V. It has been determined that the formation of ZnWO@sub 4@ was responsible for the emission of blue light.@footnote 2@ The device design to implement the blue phosphor is based on the design provided by L. D. Karpov.@footnote 3@ For the emission of electrons to excite phosphors, emitters have been fabricated by a combination of metal-carbon-metal layers as the lateral edges of wells formed in a dielectric material. Phosphors are fabricated at the bottom of the wells above anode lines. The fabrication steps of the blue light emitting lateral edge emitter along with phosphor characterization, efficiency measurements, and current-voltage characterization are presented in this paper. @FootnoteText@@footnote 1@Technology Disclosure to TAMU Technical Licensing Office (1993). @footnote 2@J. B. Sobti, P. M. Babuchna, V. Bhatia, M. H. Weichold. Paper presented at Spring, 1999, MRS meeting. @footnote 3@L. D. Karpov, V. A. Dratch, V. S. Zasemkov, A. P. Genelyev, Y. V. Migorodsky, and S. B. Proskournin. Technical digest of the 6th International vacuum Microelectronics Conference, Newport, RI, 1993.

FP-TuP2 Optical Filters for Plasma Display Panels using Organic Dyes and Sputtered Multilayer Coatings*, T. Okamura,* *S. Fukuda, K. Koike, H. Saigou, M. Yoshikai, M. Koyama, T. Misawa, Y. Matsuzaki,* Mitsui Chemicals, Inc., Japan

We describe optical filters for plasma display panels (PDP). PDP emit strong electromagnetic (EM) radiation and intense near-infrared light (NIR). The EM radiation is limited by regulations, and NIR emission causes malfunctions of devices working through NIR. The essential constituents of the developed optical filter are sputtered multilayer coatings and dye-containing layers. The sputtered multilayer coatings comprising alternate layers of metal and high-refractive material show both EM shielding effect and NIR cut-off ability without sacrificing high visible-light transparency. In addition, their reflectance should be reduced in order to improve viewability. Therefore the multilayer coatings are designed by utilizing optical admittance loci and the admittance diagrams to minimize interfacial reflection between the multilayer and the polymeric layer adjacent to it which protects the multilayer coatings and is used for adhering polymeric film such as an anti-reflection film. We obtained 7-layer (Silver and Indium-Tin-Oxide) coatings on polyethylene terephthalate substrates by roll-to-roll process, with surface resistance of 2.2@ohm@/sq., NIR transmittance of 1~12 % in 800~1200nm, visible-light transmittance > 74%, and interfacial reflectance < 0.5%. Since transparent colors of these coatings are usually greenish, we used dyes to neutralize the transparent color. The dyes are also applied to control color temperatures and minimum perceptible color differences of PDP. For this purpose, we have also developed a software tool to simulate optical designs for a given emission spectrum of PDP. The performance of this tool will be also presented.

FP-TuP3 Fabrication of a Planar Field Emitter Array on the Diamond Like Carbon Layer*, **D.H. Lee**, D.W. Kim,* Sungkyunkwan University, Korea*; S.I. Kim,* Skion Corporation, Korea*; G.Y. Yeom,* Sungkyunkwan University, Korea

Diamondlike carbon(DLC) based field emitters can be practically important in the fabrication of field emission display not only due to the properties possessed by diamond such as electronegativity, thermal stability, mechanical hardness, and chemical inertness but also due to the possibility of low temperature deposition and large area deposition. In this study, a novel DLC-based field emission device based on a planar field emitter has been designed and fabricated and its electrical properties were investigated. To maximize the field emission of the planar type field emitter, the shape and dimension of the device were simulated using a simulation tool. The deposition technique of DLC layer is very important because it can vary the emission properties of the fabricated DLC field emitter. To obtain desirable properties of DLC layer, a novel Cs ion assisted magnetron sputtering deposition technique developed by SKION Inc. was used to deposit the DLC layer at room temperature. The room temperature deposited DLC layer showed mechanical and electrical properties close to diamond The fabricated planar type DLC-based field emission device was consisted of DLC/bottom electrode/insulator/top electrode. The bottom electrode has a circular opening to expose the field emitting DLC layer. The slope of the bottom electrode opening, the thickness of the insulator layer, and the opening of the top electrode in addition to their materials were optimized to obtain a stable FED structure and the necessary electric field for electron emission and convergence of the electron beam. Details of the fabrication techniques and the electrical properties of the fabricated field emission devices will be discussed. Also, the properties of DLC layer deposited by Cs ion assisted magnetron sputtering will be also discussed.

FP-TuP4 Effects of ZnO Buffer Layer on the Luminous Properties of Thin Film Phosphors Deposited on ZnO/ITO/Glass Substrate*, **Y.J. Kim**, Y.H. Jeong, S.M. Jeong,* Kyonggi University, Korea

Thin film phosphors deposited on ITO(Indium tin oxide) coated glass panel have a disadvantage of lower cathodoluminescent brightness than powder types due to the poor crystalline quality. It is very difficult for thin film phosphors to have high quality crystal structures, because ITO has an amorphous like structure. To improve the cathodoluminescent properties of thin film phosphors, ZnO buffer layer was deposited by sputtering methode between thin film phosphors and ITO coated glass substrate. All thin film phosphors were deposited by rf magnetron sputtering method. Transparent c-axis preferentially oriented ZnO thin film buffer layer could be obtained on ITO thin film, while ITO had an amorphous like structure. ZnGa@sub 2@O@sub 4@:Mn and CaTiO@sub 3@:Pr thin film phosphors were used to evaluate the effects of ZnO buffer layer. The crystal structures of thin film phosphors deposited on ZnO/ITO/glass substrate were developed better than those on ITO/glass, consequently the formers showed cathodoluminescent intensity at least twice as high as the latter. CaTiO@sub 3@:Pr and ZnGa@sub 2@O@sub 4@:Mn thin film phosphors showed sharp CL emissions at 613nm and 509nm, respectively.

FP-TuP5 Investigation of the Outgassing Characteristics of the Materials Consisted of Plasma Display Panel*, **H.R. Han**, Y.J. Lee, G.Y. Yeom,* Sungkyunkwan University, Korea

In the fabrication of PDP, before filling with light emitting gases (Xe+Ne, etc.) to the fabricated panel, the panels are exhausted through a small section glass pipe attached to one side of the rear glass substrate of the panel. Currently, this gas exhausting takes more than several hours to obtain a desirable vacuum state of around 10@super -7@Torr due to the outgassing from the materials inside of the panel. It is known that this gas exhausting process is one of the most time-consuming processes that reduces the production rate and increases the cost of PDP. However, at present, the affecting factors or the materials causing the severe outgassing from the panel during the exhausting are not well understood due to the variety of materials and complex processing involved in the fabrication of the PDP. In this study, outgassing characteristics of the materials consisted of PDP and PDP panel itself were systematically studied using a thermal desorption technique to understand the origin of the severe outgassing. The characteristics of outgassing were investigated as a function of time and temperature. As the investigated materials, electrode(metal, ITO), dielectric films, barrier rib, fluorescent films, protective layer(MgO), and frit on the glass panel and the multilayer of these materials consisted of PDP panel were used and they were heated up to 500°C. Also, these materials were kept at 350°C for a few hours to measure outgassing characteristics at 350°C which is the temperature used for the exhausting process in the fabrication of PDP. The result showed that the maximum outgassing temperature from the single materials was varied from 100°C to 150°C. Mass spectrometry measurements of the materials maintained at 350°C have shown that the severe outgassing is primarily related the MgO and fluorescent films. These behaviors were compare with outgassing from the complete panel.

FP-TuP6 Characterization of Radio Frequency Magnetron Sputter-deposited Ga@sub 2@O@sub 3@:Mn Phosphors of Thin Film Electroluminescent Display Devices*, J.S. Lewis, **J.H. Kim**, P.H. Holloway,* University of Florida

Manganese-activated Ga@sub 2@O@sub 3@ phosphor thin films as the emitting layer of alternating current thin film electroluminescent (ACTFEL) display devices have been prepared by radio frequency (rf) magnetron sputtering of a Mn-doped Ga@sub 2@O@sub 3@ target in a pure argon or an oxygen-argon mixture atmosphere. The structural and compositional properties of the deposited Ga@sub 2@O@sub 3@:Mn phosphor thin films have been systematically investigated as a function of the sputter deposition parameters, such as rf power, working pressure, oxygen gas concentration, and substrate temperature ranging 5 - 50 W, 5 - 30 mTorr, 0 - 50 %, and room temperature - 400 °C, respectively. The surface morphology, structure, and composition of the deposited Ga@sub 2@O@sub 3@:Mn films were characterized by atomic force microscopy (AFM), scanning electron microscopy (SEM), X-ray diffraction (XRD), and energy dispersive X-ray spectroscopy (EDS). Their electroluminescent and photoluminescent characteristics were also evaluated and correlated with the results of the structural and compositional analyses. The ACTFEL display devices were fabricated using the conventional structure, Al/BTO/Ga@sub 2@O@sub 3@:Mn/ATO/ITO/glass, and the inverted structure, ITO/BTO/Ga@sub 2@O@sub 3@:Mn/PZT/Au/Al@sub 2@O@sub 3@.

FP-TuP7 Fabrication of a Microchannel Plate for a FED by Solution-based Multilayer Thin Film Coating*, **S. Yu**, T. Jeong, J. Lee, S. Jin, W. Yi, J. Heo, J.M. Kim,* Samsung Advanced Institute of Technology, Korea

To develop a high efficient field emission display (FED), a special microchannel plate (MCP) was incorporated in a FED, where field-emitted electrons are amplified in the cylindrical holes of a MCP by action of secondary electron emission from the emissive layer, and MCP characteristics are examined. We fabricated an alumina-based MCP with many micrometer-sized cylindrical holes by computerized punching and firing of the laminated alumina green sheet, where the aspect ratio of the hole was chosen to be around 13. Solution-based hybrid layer coating was utilized for MCP fabrication. Cu electroless coating was applied to a MCP, then Cu layer was oxidized to be a conductive layer on the surface of the hole. Tetraethyl orthosilicate (TEOS) containing solution was spin coated on the copper oxide layer. Consequent firing resulted in a SiO2 thin layer as an emissive layer. Then electrodes on the two faces of a MCP were deposited by an e-beam evaporator. To optimize the MCP fabrication process, we followed the design of experiment (DOE) scheme. We chose three DOE factors: Cu layer thickness controlled by the Cu electroless coating time (10 and 15 minutes), Cu oxidation temperature (570, 800, and 1030 C), and TEOS concentration (0.015 M and 0.007 M) for SiO2 layer thickness. We measured the current amplifying gain of our MCP by an e-gun. The highest gain was obtained to be about 10 for the sample with 15 min Cu coating time, 1030 C oxidation temperature, and 0.007 M TEOS concentration, where this gain will be beneficial for a new kind of FED by increasing the intensity of cathodoluminescence. Further experiments by varying other experimental factors are undergoing, and good results are expected.

Material Characterization
Room Exhibit Hall C & D - Session MC-TuP
Poster Session

MC-TuP1 Quantitative Detection and Mapping of SiOH Groups on Si using Chemically Labeled TOF-SIMS Method*, **T. Mitsuoka**, M. Ikai, T. Ohwaki, Y. Taga,* TOYOTA Central Research and Development Laboratories Inc., Japan

This paper first demonstrates an accurate quantitative detection and mapping of SiOH by Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS) combined with phenyldimethylchlorosilane (PDMCS) treatment to detect the amount of SiOH on a Si wafer. We found that we can detect the quantity of SiOH on a Si wafer without the influence of adsorbed water by the labeled TOF-SIMS method. Furthermore, we could map the 2D distribution of SiOH on the Si surface. The quantitative analysis of SiOH by TOF-SIMS was confirmed as follows. H and OH terminated surfaces were prepared by dipping a Si wafer into hydrofluoric acid (HF) solution and H@sub 2@O@sub 2@:H@sub 2@SO@sub 4@=4:1 solution, respectively. Contact angles of the SiOH surface became smaller with dipping time in deionized water. Surface chemical characteristics and adhesion force of the surfaces thus treated were examined by attenuated total refraction (ATR) of IR and Atomic Force Microscopy (AFM). The yields of characteristic ions (C@sub 6@H@sub 5@Si@super +@, C@sub 6@H@sub 5@(CH@sub 3@)@sub 2@Si@super +@)emitted from the labeled SiOH surfaces were compared with the data of contact angles, ATR and AFM. There was a good correlation between the amount of these fragment ions and contact angles. In conclusion, quantitative detection and mapping of SiOH groups on Si were demonstrated by the sophisticated labeled TOF-SIMS method.

MC-TuP2 Secondary Ion Emission from Well Defined Molecular Overlayers Under Molecular Primary Ion Bombardment*, **D. Stapel**, A. Benninghoven,* University of Muenster, Germany

Molecular primary ions have been shown to enhance the yield Y(X@sub i@@super q@) of organic secondary ions considerably. The simultaneous increase in the corresponding damage cross section @sigma@(X@sub i@@super q@) is much smaller. This holds in particular for thick molecular samples like LB multilayers or polymers. For LB multilayers we found yield increases up to a factor of 1000, when changing from Ar@super +@ to SF@sub 5@@super +@ bombardment. This phenomenon is important for practical analytical applications of TOF-SIMS, because yields, damage cross sections, and the resulting ion formation efficiencies E=Y/@sigma@ determine the achievable sensitivity as well as the achievable lateral resolution. In recent years we have investigated in some detail this secondary ion emission behavior for a variety of LB layers under atomic and molecular primary ion bombardment. Basic studies were performed with three series of LB layers (n = 1, 3, 5, 7, 9; n : number of monolayers) under 0.5 - 11 keV Ne@super +@, Ar@super +@, Xe@super +@, O@sub 2@@super +@, CO@sub 2@@super +@, SF@sub 5@@super +@, C@sub 7@H@sub 7@@super +@, C@sub 10@H@sub 8@@super +@, C@sub 6@F@sub 6@@super +@ and C@sub 10@F@sub 8@@super +@ bombardment. Y(X@sub i@@super q@) as well as @sigma@(X@sub i@@super q@) were determined. We found a more pronounced Y and E enhancement for multilayers (n>1). Y, @sigma@ and E increases with increasing mass of atomic primary ions and with growing number of constituents up to 6 heavy atoms. Y, @sigma@ and E features a saturation behaviour for molecular primary ion species containing more than 6 atoms. We could not find an influence of the chemical composition of the primary ion on this enhancement under static SIMS conditions. We found that the molecular secondary ions are emitted from the 1@super st@ and 2@super nd@ layer and a pronounced decrease in Y and E was determined for 1 keV SF@sub 5@@super +@ bombardment.

MC-TuP3 A SIMS Study on the Negative Boron Cluster Secondary Ion Yield Change in Boron Implanted Silicon*, **S. Hayashi**,* Nippon Steel Corporation, Japan*; Y. Okamoto,* SHARP Corporation, Japan*; F. Toujou,* Matsushita Technoresearch Inc., Japan*; Y. Homma,* NTT Basic Research Laboratories, Japan

To establish standard protocols in depth profiling, the linearity of the ion intensity using the ion-implanted silicon specimens with a variety of ion dose have been investigated. In these round-robin test, we have been studying secondary ion emission mechanism and found the irregularity of the production of negative boron cluster in boron implanted silicon specimens. These phenomena have been reported only the positive secondary ion emission in the high dose specimen.@footnote 1@ In this study we applied the boron implanted silicon wafer to quantify the amounts of boron in silicon with a wide concentration range. Cs@super +@ ion beam was used to detect negatively charged boron cluster ion signals, ie, B@super -@, B@sub 2@@super -@, B@sub 3@@super -@ ,etc.. The dependency of negative secondary ion yields on a variety of ion doses was estimated in order to compare with the detection of boron cluster ion counts. The higher dose of boron was implanted into silicon, the larger production efficiency of boron cluster ion was. Especially, the efficiency of B@sub 2@@super -@ exceeded the one of boron atomic ion in the high dose, 1x10@super 17@ions/cm@super 2@ specimen which was implanted B@super +@ with 50keV as an accelerating voltage. Such an enhancement of negative dimer ion emission yield cannot be explained on the basis of the recombination mechanism because B@sub 2@@super -@ yield is larger than the B@super -@ ion yield. The emission mechanism of boron negative cluster ion will be discussed, comparing with the dependence of the boron negative cluster ion yields on the implanted doses, the shape of the implanted depth profile, and boron positive secondary ion emission. @FootnoteText@ @footnote 1@M. Tomita, F. Takahashi and Y. Homma, Nucl. Instrum. Methods Phys. Res., B85(1994), 399.

MC-TuP4 Fabrication and Characterization of Boron-Doped Silicon Thin Film as a Reference Material for Secondary Ion Mass Spectrometry Quantification*, **K.J. Kim**, D.W. Moon, H.K. Kim,* Korea Research Institute of Standards and Science, Korea*; C.J. Park,* Korea Research Institute of Standards and Science

Secondary ion mass spectrometry(SIMS) is one of the most powerful techniques for the determination of the concentration of minor impurities in solid materials. Ion implanted reference materials are generally used for the quantification of impurities by SIMS. In this study, we will present a new type of reference material for the quantification of minor impurities by SIMS. Uniformly-doped silicon thin films with three levels of boron concentrations were fabricated by ion beam sputter deposition. A Si target with a small BN was sputter deposited simultaneously on a Si(100) and a polyester substrate by 1 keV Ar ion beam. The boron concentration was determined by inductively coupled plasma mass spectrometry (ICP-MS) using the isotope dilution method. The boron concentration measured by ICP-MS was compared with that by SIMS using a boron ion implanted standard reference material.

MC-TuP5 Development of Secondary Ion Mass Spectrometry Methodology for the Film Thickness Measurement of Sub-2nm SiO@sub 2@ Interlayers*, C.M. Jones, **J. Zhao**,* Advanced Micro Devices

Film thickness of interfacial SiO@sub 2@ in poly-emitter devices and thickness of gate oxide in transistors is crucial to device performance and speed. The thickness regimes (0-1nm and 1.5-2.5 nm, respectively) are too thin to allow for accurate measurement by electron microscopic techniques. In the present work, we report the development of secondary ion mass spectrometry (SIMS) methodology for the film thickness measurement of sub-2nm SiO@sub 2@ interlayers. The SiO@sub 2@ interlayer structure is polycrystalline Si / SiO@sub 2@ / Si substrate. The polycrystalline Si layer can be up to a few hundred nano-meters thick. The sample is analyzed by SIMS and a concentration depth profile of oxygen is acquired. High-energy Cs bombardment is used, so that the thin SiO@sub 2@ layer is diluted by ion beam mixing. A 14.5 kV net impact energy provides sufficient mixing to change the composition of the interface from that of stoichiometric SiO@sub 2@ to Si with a high dose of oxygen. The areal density of the interfacial oxygen peak may be calibrated against a SIMS oxygen ion implant standard with a precision of better than 3%. The SiO@sub 2@ thickness is then calculated with equal precision, using the formula derived. A statistical measurement of the same sample over a period of several weeks demonstrated a superior reproducibility.

MC-TuP6 Analysis of Delta Multilayer Profiles Measured by Secondary Ion Mass Spectrometry*, **A. Takano**, Y. Higashi,* NTT Advance Technology Corporation, Japan*; Y. Homma,* NTT Basic Research Laboratories, Japan*; J. Kikuma, S. Soga, Y. Okamoto, R. Oishi, S. Hayashi, R. Saito, M. Tomita, Y. Ueki, S. Seo, F. Toujou, S. Yoshikawa, J. Kinoshita,* SIMS-Depth Profiling WG, Japan*; D.W. Moon,* Korea Research Institute of Standards and Science, Korea

Delta-doped multilayers are potential reference materials for the evaluation of depth resolution in secondary ion mass spectrometry (SIMS). For this purpose establishing standard procedures of depth resolution evaluation is necessary, as well as developing reliable delta multilayers. We tested a theoretical model, mixing-roughness-information depth (MRI) model@footnote 1@ for extracting depth resolution parameters from the measured profiles in the round-robin study using a delta-multilayer specimen that includes five GaAs-doped delta layers separated by amorphous Si layers. The measured arsenic profiles were analyzed using the MRI model. For SIMS, information depth in the model can be regarded to be very small, so we used the only two parameters concerning mixing and roughness. The mixing parameters showed very little in-depth variation but dependence only on primary-ion energy and impact angle, irrespective of the instrument types used. This means that the mixing parameter may be regarded as a physical quantity. The roughness parameter and its in-depth dependence, on the other hand, varied among participating laboratories, reflecting the measurement conditions and surface roughening. @FootnoteText@ @footnote 1@ S. Hofmann, Surf. Interface Anal. 21 (1994) 673

MC-TuP7 Comparison of Improved Spreading Resistance Profiling and Secondary Ion Mass Spectrometry in the Characterization of Ion Implanted Dopant Profiles*, **L.C.P. Tan**,* The National University of Singapore, Republic of Singapore*; L.S. Tan, M.S. Leong,* The National University of Singapore*; C.W. Lee,* ST Microelectronics Ltd.

Spreading resistance profiling (SRP) is a well-established technique for the determination of dopant profiles in silicon wafers. The dopant profile can then be recovered from the spreading resistance profile by using an iterative algorithm. It has been noticed that for certain dopant profiles, especially shallow ion implanted profiles, the junction depth determined from SRP often do not agree with those predicted by process simulators such as SUPREM3. In addition, the sheet resistance as measured using four-point probes is also sometimes different from that deduced from dopant profiles recovered by SRP. The discrepancy may arise if the algorithm used to convert the spreading resistance profile into the dopant profile does not take into an account a phenomenon known as the carrier redistribution effect. In this work, we describe the results of a set of experiments carried out to compare the dopant profiles obtained from SRP and secondary ions mass spectrometry (SIMS) as well as those predicted by SUPREM3. SRP is an electrical characterization technique that responds to the presence of electrons and holes. The p-n junction indicated by the spreading resistance profile is the electrical junction, where the electron concentration is equal to the hole concentration. SIMS, on the other hand, is a physical characterization technique that measures the profile of dopant atoms, and the junction obtained by SIMS is the metallurgical junction where the donor concentration is equal to the acceptor concentration. The electrical junction and the metallurgical junction do not necessarily coincide because of the carrier redistribution effect, especially in shallow ion implanted profiles. However, we shall show that by using a new algorithm that correctly models the carrier redistribution effect, the disagreement in the dopant profiles obtained by SRP, SIMS and SUPREM3 can be significantly reduced.

MC-TuP8 Characterization of Si Distribution at the Tungsten / Titanium Nitride Interface Using Secondary Ion Mass Spectrometry - An Investigation of the Dynamic Response of a Chemical Vapor Deposition Chamber*, **C.M. Jones**, J. Zhao,* Advanced Micro Devices

In sub-micron MOS IC processing, tungsten lines or contact (via) plugs are formed by blanket chemical vapor deposited tungsten thin film fill into the narrow SiO@sub 2@ trenches or small contact openings on the titanium nitride (TiN) layer with the underlying structure. The blanket CVD tungsten thin film is typically accomplished as the following: a thin nucleation layer (~50nm) is grown by silane (SiH@sub 4@) reduction of tungsten hexafluoride (WF@sub 6@), and the bulk deposition is accomplished via hydrogen (H@sub 2@) reduction of WF@sub 6@. The TiN layer serves as an adhesion layer that promotes uniform W growth as well as a diffusion barrier between W and underlying Si or silicide layers. For the common CVD deposition chamber, such as a batch-processing machine, the deposition process parameters, such as gas flow, temperature and pressure, are monitored in the inlets of the chamber usually at a distance from the wafer surface where the reaction takes place. The small SiH@sub 4@ gas flow that controls the Si concentration in the nucleation layer, in particular, will have certain modulating effects from the chamber, in terms of time and concentration, in the course of transport. In the present work, simultaneous SiH@sub 4@ and H@sub 2@ reduction of WF@sub 6@ formed the tungsten nucleation layer with a nominal thickness of 60nm. A two-step SiH@sub 4@ gas flow scheme was used to determine the effects of magnitude and duration of SiH@sub 4@ flow on the Si concentration at the W/TiN interface. The results amply demonstrate that SIMS analysis can be used to evaluate the deposition process so as to meet the fill and barrier protection requirements for narrow trench or small via. Issues of SIMS analysis such as depth resolution, interference from molecular ions, memory effect, and quantification are discussed.

MC-TuP9 SIMS/XPS Depth Profiling of a Fluoride-Modified Epoxycoating*, **W.J.H. Van Gennip**, R.D. Van de Grampel, R. Van der Linde,* Eindhoven University of Technology, The Netherlands*; P.C. Zalm,* Philips Research, The Netherlands*; J.W. Niemantsverdriet,* Eindhoven University of Technology, The Netherlands, Netherlands

The surface of an epoxy resin has been modified by the addition of a small amount of a polymerizable monomeric surfactant. The difference between the surface free energy of the epoxy and surfactant caused the surfactant, by definition the component with the lower surface free energy, to segregate preferentially to the solid/air interface. Curing caused the surfactant to bind to the crosslinking agent, thus permanently modifying the surface of the epoxy. Initial XPS measurements showed that the surface is indeed fluoride-modified. This was confirmed by contact angle measurements. Only a small amount of surfactant is necessary to saturate the surface. These exploratory measurements were used as reference to study, explain and confirm the depth profiles we subsequently acquired using depthprofiling SIMS. Although depth profiling of semiconductors has become a widely used technique, the application of depthprofiling SIMS to polymers is much less common. The preliminary results obtained thus far indicate that depthprofiling through polymers can deliver useful results unobtainable by other techniques.

MC-TuP10 Strategies for Reducing the Effects of Topography in Depth Profile Analysis of Polycrystalline Thin Film CdTe/CdS Photovoltaic Materials and Devices*, **S.E. Asher**, M.R. Young, H. Moutinho, T. Gessert, R.G. Dhere, P. Sheldon,* National Renewable Energy Laboratory

Polycrystalline thin film materials are promising for low-cost, large area manufacturing of photovoltaic modules. Surface analysis methods are critical tools to measure the distribution of contaminants and dopants in these materials. However, the native topography and heterogeneity can present significant challenges for depth profile analysis, particularly by SIMS. We have developed several methods that have proved useful for SIMS examinations of CdTe/CdS solar cells made by different thin film deposition methods. Depth profile results obtained after chemical etching, controlled polishing and back-side analysis show strengths and limitations of each method. These methods have allowed us to study diffusion and composition in 100 nm CdS layers buried under up to 10 µm of CdTe. In the films studied, the CdTe may have an initial average surface roughness of @>=@ 200 nm or more. The depth profile results from sample preparation methods listed above will also be compared to depth profiles obtained with sample rotation. We find that sample rotation in these materials is complicated by lateral inhomogeneities, even when the rotation speed is well matched to the cycle time of the analysis.

MC-TuP11 Comparison of Sputter Rate and Interfacial Resolution in a Multi-instrument Surface Science Laboratory*, **M.H. Engelhard**, A.S. Lea, D.J. Gaspar, G.C. Dunham, T. Thevuthasan, D.R. Baer,* Pacific Northwest National Laboratory

A multi-instrument, multi-technique laboratory faces a wide variety of analysis needs. Although much is known about the parameters that influence sputtering and the ability of a technique to resolve an interface, variations among different instruments reflect the geometry and design of each instrument, as well as the conditions convenient for operation and actual performance of an ion gun. Each instrument has advantages and limitations for specific types of analyses. In order to determine the actual performance of various instruments found in the Environmental Molecular Sciences Laboratory, we have measured interfacial resolution and sputtering rates produced for common operating and a few optimized sputter conditions for several instruments. The capabilities of these instruments include X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), time-of-flight secondary ion mass spectrometry (TOF-SIMS), and accelerator based materials analysis. Samples used for these studies included Si/SiO@sub 2@, Ta/Ta@sub 2@O@sub 5@ and Ni/Cr multilayer standards. For instruments with sample rotation capability, data has been collected with and without rotation. Using this data, we have developed a matrix describing the performance of the various techniques and instruments. We utilize this matrix to choose the appropriate instrumentation to acquire the desired information at the required accuracy for a wide range of scientific studies in the minimum time.

MC-TuP12 XPS Investigation of Counterion Exchange in SiO@sub 2@ Sol-gel Films Doped with Tris(2,2'-bipyridine)Ruthenium(II)*, **X. Wen**, M. Sykora, T.J. Meyer, R.W. Linton,* University of North Carolina at Chapel Hill

SiO@sub 2@-based sol-gels provide an attractive matrix for doping a variety of molecules. Ru complexes are among the most attractive dopant molecules for SiO@sub 2@ sol-gels due to their unique photophysical and redox properties. Applications of sol-gel films doped with Ru complexes are mostly based on the properties related to the metal-to-ligand charge transfer (MLCT) excited state of the complex. The MLCT excited states are very sensitive to not only the physical nature but also the compositions of the sol-gel matrix. This research work investigates the possible new method of tailoring the compositions of SiO@sub 2@ sol-gel thin films doped with [Ru(bpy)@sub 3@]Cl@sub 2@, which involves the exchange of the original counterions of Ru complexes with new counterions. SiO@sub 2@ sol-gel films doped with [Ru(bpy)@sub 3@]Cl@sub 2@ were prepared by spin-coating from sol/[Ru(bpy)@sub 3@]Cl@sub 2@ mixtures. XPS coupled with Ar@super +@ sputtering was used to study both the surface compositions and depth profiles of the sol-gel films before and after the counterion exchange experiments. The results indicated the original counterion, Cl@super -@, of Ru(II) complex completely leached out of the film after exposing the film to water. Cl@super -@ ion could be reintroduced into the film by putting the Cl@super -@ deprived film back in HCl solution. New counter ions, such as PF@sub 6@@super -@, were incorporated into the sol-gel film by immersing the Cl@super -@ deprived film in HPF@sub 6@ solution. The incorporation of PF@sub 6@@super -@ ions was both time and pH dependent. In addition, cations such as Na@super +@ could also be incorporated into the film by putting the sol-gel film in basic solutions such as Na@sub 2@HPO@sub 4@/NaH@sub 2@PO@sub 4@. This approach was used to calculate the ratio of total Si to the number of SiO@super -@H@super +@ sites that can be exchanged in the SiO@sub 2@ sol-gel films.

MC-TuP13 SiO2 Growth on Si(100) and (111) Investigated by QUASES-XPS Analysis*, **B. Semak**, C. Gundlach, P. Morgen,* University of Southern Denmark*; S. Tougaard,* University of Southern Denmark, Denmark

It is well known that the growth of SiO2 on Si is an activated process. It must involve heating and it may be strongly influenced by the presence of small amounts of catalysts like alkali metals. A fundamental problem for the growth of very thin SiO2 films with heating is the formation of oxide islands and trenches at their perimeters. The parameters of oxide growth are varied in a series of experiments to determine their influence on the morphology and interface structure of silicon oxide on Si(111) and Si(100). Here we have used the QUASES-XPS technique@footnote 1@ to analyze the surface morphologies of 0 to 10 nm thin SiO2 films. The SiO2 growth is determined for different cycles of alkali-metal evaporation-, oxygen exposure- and annealing- procedures. @FootnoteText@ @footnote 1@ http://www.quases.com.

MC-TuP14 Influence of Ar@super +@ Ion Bombardment on the Chemical States of SrBi@sub 2@Ta@sub 2@O@sub 9@ Thin Films Fabricated by Metal-Organic Decomposition*, **Y.B. Park**, K.Y. Min, S. Heo, C.H. Lim, M.K. Lee, H.J. Kim, S.Y. Lee,* Hyundai Electronics Industries Co., Ltd., Korea

SrBi@sub 2@Ta@sub 2@O@sub 9@(SBT) belongs to a Bi-layered perovskite structure where double Ta-O octahedron layers are sandwiched between (Bi@sub 2@O@sub 2@)@super 2+@ layers were analyzed for the characterization of chemical states with the help of x-ray photoelectron spectroscopy (XPS) during the depth profiling analysis. When the sputter etching was performed to SBT films by Ar@super +@ ion bombardment, the chemical states of constituents were changed as a function of the applied Ar@super +@ ion beams energy from 1kV to 4kV. Among the constituents of SBT film, the Sr 3d peak was slightly changed by the change of Ar@super +@ ion beams energy. On the other hand, the change of Ta 4f and Bi 4f peak were obviously dependent on the applied Ar@super +@ ion beams energy. In particular, Bi 4f peak was dramatically changed from Bi@sub x@O@sub y@ oxide states to Bi metallic states by the lower Ar@super +@ ion energy than the cases of Sr and Ta. These changes of chemical state within SBT film resulted from the preferential sputtering of oxygen atoms. Following out present study, Preferential sputtering of oxygen atoms was found to depend on thermal stability and mass difference between oxygen and each constituent within SBT film.

MC-TuP15 XPS Analysis of Plasma-Modified Polymers for Enhanced Cellular Response*, **R. White**,* VG Scientific, UK*; R.L. Williams, T. Markkula,* University of Liverpool, UK*; G. Jones, J. Wolstenholme,* VG Scientific, UK

Gas plasmas are a convenient way of modifying the surface properties of polymers without significantly altering their bulk properties. As such they have been proposed as a means of modifying the surface properties of polymers to enhance the cellular response to the materials for particular applications. XPS has been used to determine both the elemental composition and chemical state functionality of PET and PTFE polymers modified using two different RF plasma systems (Capacitor Plate and Inductive Coil) with nitrogen and ammonia gases. Initial results indicate significant differences in modification of the polymers with the respective treatments.

MC-TuP16 Surface Potential Measurement with High Spatial Resolution using a Scanning Auger Electron Microscope*, Y. Sakai, M. Kudo,* JEOL Ltd., Japan*; **C. Nielsen**,* JEOL USA Inc.

The microscopic surface potential distributions were measured from the onset energies of secondary electron spectra using a scanning Auger electron microscope. An equipment used in this experiment was a scanning Auger electron microscope (JEOL Model JAMP-7830F) attached with a hemispherical electron energy analyzer with an input focusing lens system and a secondary electron detector to take SEM images. The electron gun is a Schottky field emission type and electrons emitted from a cathode tip are focused onto the specimen surface. The hemispherical electron energy analyzer with a high detection efficiency in the region lower than several ten eV was used at an ultra-high vacuum pressure. Such a technology makes possible to measure the work function change caused by different crystal orientations, the surface potential profile depending on micro-electronic structures of semiconductor devices, etc. The typical applications of the work function measurement are presented in this paper. The four grains of poly-crystal Ni (99.9% purity) with different crystal orientation were prepared for testing a spatial resolution of work function mapping. The initial rises of secondary electron emission for the four grains of Ni are observed by the primary electron beam at 10 keV and 1.3 n A., and the onset energies are 5.55, 5.60, 5.65, and 5.50eV, respectively. If we put the work function of the analyzer equal to 5.60 eV, the work functions of Ni are 4..95, 5.04, 5.22 and 5.35 eV, respectively. The mapping of work function distribution was carried out by measuring intensities of secondary electron emission at the fixed point of. 5.70eV. The observed work function images show a spatial resolution of several tens nm estimated from the image contrast. The measurement of work function and imaging of the surface potential at a spatial resolutions of several tens nm and a sensitivity of 0.05V have been established by using a scanning Auger electron microscope of ultra-high vacuum.

MC-TuP17 Satellite Structure of KLL Auger Spectra in Fluorides*, **L. Kövér**,* Institute of Nuclear Research of the HAS, Hungary*; M. Uda,* Waseda University, Japan*; I. Cserny, J. Tóth,* Institute of Nuclear Research of the HAS, Hungary*; K. Ogasawara, H. Adachi,* Kyoto University, Japan

Considerable chemical effects have been found on the satellite structures of the F KLL Auger spectra in fluorides recently,@footnote 1-3@ which could be important for surface chemical identification and could provide information on the origin and the atomic or molecular character of the particular Auger satellite lines. In the case of the alkali fluorides unassigned satellites were found and interpreted on the basis of a new concept,the resonant orbital rearrangement.@footnote 3@ In the present work we study the structure of the Auger satellites induced from rutile-type fluorides. F KLL Auger spectra were excited by Al K@alpha@ and Cu L@alpha@ X-rays from polycrystalline powder samples of MgF@sub 2@, ZnF@sub 2@, NiF@sub 2@ and CoF@sub 2@ and measured by a high luminosity electron spectrometer.@footnote 4@ Excitation by Cu L@alpha@ increased the peak to background ratio in the spectra significantly. Similarly to the alkali fluorides, a satellite has been found in the high kinetic energy part of the measured F KLL spectra. From the satellite intensities the fluorescence yield for the doubly ionized states in MgF@sub 2@ has been determined. An inverse proportionality has been found between the satellite/diagram X-ray and the corresponding Auger intensity ratios, while the latter ratios have been found to be proportional to the energy width of the new Auger satellites. These observations indicate the resonant nature of the Auger transition identified. For determining the energy difference between the molecular orbitals in resonance, Discrete Variational X@alpha@ cluster molecular orbital calculations have been performed. This work was supported by the projects OTKA T026514, MTA-JSPS 24/1998. @FootnoteText@ @footnote 1@ O. Benka and M. Uda, Phys. Rev. Letters, 56 (1986) 1667, @footnote 2@ H. Aksela, E. Kukk, S. Aksela, A. Kikas, E. Nommiste, A. Ausmees and M. Elango,Phys. Rev. B 49 (1994) 3116,@footnote 3@ M. Uda, T. Yamamoto and T. Takenaga, Adv. in Quant. Chem. 29 (1997) 389,@footnote 4@ L. Kövér, D. Varga, I. Cserny, J. Tóth and K. Tökési, Surf. Interface Anal. 19 (1992) 9.

MC-TuP18 XPS and XRD Characterization of CuO-TiO2-CeO2 Catalyst System*, M.S.P. Francisco,* Universidade de Sao Paulo, Brazil*; **P.A.P. Nascente**,* Universidade Federal de Sao Carlos, Brazil*; V.R. Mastelaro,* Universidade de Sao Paulo, Brazil*; A.O. Florentino,* Universidade Estadual Paulista, Brazil

The CuO-TiO@sub 2@ system has been widely studied due to its catalytic properties on methanol oxidation. However, disadvantages are related to TiO@sub 2@ as support: thermal instability, its sintering and the sintering of the active phase. The cerium addition to this system is known to stabilize the active phase in a fine dispersed state and to improve both the resistance to thermal loss of surface area and the catalytic activity of supported catalysts. The influence of loading cerium and cooper to TiO@sub 2@ on its superficial composition and on its structure have been studied by X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD) and X-ray absorption spectroscopy (XAS). The analyses revealed that with increasing amount of cerium on titania, cerium occurs mainly in a dispersed superficial specie and just a little as CeO@sub 2@ phase (cerianite). At higher loading of cerium, the CeO@sub 2@ phase increases and the Ce/Ti atomic rate is smaller than the bulk rate, as a consequence of cerium agglomeration. We have concluded that a limited amount of cerium can be spread on the titania surface. The Cu/(Ce+Ti) atomic rate showed no influence from cerium on the dispersion of cooper. For CuO-TiO@sub 2@ samples with low concentration of cerium, we could observe that cerium is found as Ce@super 3+@, at least partly. Also the XPS spectra confirmed the presence of a second titanium specie with a spin-orbit component at higher binding energy than the one presented by Ti@super 4+@ in CuO-TiO@sub 2@ samples rich in cerium. The structural results obtained by XAS were in good agreement with those obtained by XRD and XPS.

MC-TuP19 Structural Characterization of V@sub 2@O@sub 5@/TiO@sub 2@ Catalysts*, C.B. Rodella,* Universidade de Sao Paulo, Brazil*; **P.A.P. Nascente**,* Universidade Federal de Sao Carlos, Brazil*; V.R. Mastelaro, M.R. Zucchi, R.W. Franco, C.J. Magon, J.P. Donoso,* Universidade de Sao Paulo, Brazil*; A.O. Florentino,* Universidade Estadual Paulista, Brazil

Vanadia supported on titania constitutes a well-know catalytic system for selective oxidation of o-xylene, ammoxidation of hydrocarbons and selective reduction of NO@subx@ with NH@sub3@. A series of V@sub2@O@sub5@/TiO@sub2@ samples was synthesized by sol-gel and impregnation method with different contents of vanadia and treated in different calcination temperature. The samples were characterized by X-ray diffraction (XDR), X-ray photoelectron spectroscopy (XPS), Raman spectroscopy and electronic paramagnetic resonance (EPR). XDR detected rutile as the predominant phase for pure TiO@sub2@ prepared by the sol-gel method when calcined at 450@super0@C. The structure changed to anatase when the vanadia loading was increased. Also anatase was the predominant phase for samples obtained by the impregnation method. XPS results indicated that the Ti ions were surrounded tetrahedrally by oxygen ions. The V/Ti atomic ratios showed that V ions were highly dispersed on the vanadia/titania surface obtained by sol-gel method. Raman measurements identified three species of surface vanadium: monomeric vanadyl (V@super4+@), polymeric vanadates (V@super5+@) and V@sub2@O@sub5@ crystalline. EPR analysis detected three V@super4+@ ion types: two of them were located in axial symmetry sites substituting the Ti@super4+@ in the rutile structure, and the third one was constituted by a magnetically interacting V@super4+@ ions in the form of pairs or clusters. For the materials with higher concentrations of vanadium, a partial oxidation of V@super4+@ to V@super5+@ was evident from EPR analysis.

MC-TuP20 Investigation of Oxide Layers Formed on NiTi Shape Memory Alloys at Elevatated Temperatures*, **R.G. Vitchev**, G. Firstov, H. Kumar,* Katholieke Universiteit Leuven, Belgium*; Y. Liu,* Nanyang Technological University, Singapore*; B. Blanpain, J. Van Humbeeck,* Katholieke Universiteit Leuven, Belgium

NiTi shape memory alloys have attracted considerable attention as materials for medical implants. It is known that the biocompatibility of the implants fabricated from NiTi depends on their surface composition since nickel often causes allergic and toxic effects. The purpose of this study is to characterise the thermally grown oxides on the surface of an NiTi alloy (50 at. % Ni). The samples were heat treated in air in the temperature range 473-1073 K. Thermo-gravimetry measurements were carried out to investigate the kinetics of oxidation. X-ray photoelectron spectroscopy and Auger electron spectroscopy combined with sputter depth profiling were used to investigate the surface composition and chemical state of the constituent atoms and their depth distribution. X-ray diffraction was used to determine the phases formed in the oxide layers. The influence of the surface treatment of the alloy on the oxidation process was also studied. Thermodynamic calculations were carried out to explain the oxidation behaviour of the NiTi alloy.

MC-TuP21 Reduction of Artifacts in Temperature Programmed Desorption Measurements of Field Generated, Real-Life, Powdered Samples*, **V.S. Smentkowski**, A.L. Linsebigler,* General Electric Corporate Research and Development Center

Temperature programmed desorption (TPD) is a powerful surface analytical technique used for studies of adsorbate systems under controlled, high vacuum, conditions. Even under controlled, high vacuum, conditions background events such as desorption from the mounting wires and/or the heater assembly can contribute to the TPD signal and complicates data analysis. Researchers often need to determine the desorption characteristics of field generated, real-life, samples that have been prepared under ambient conditions and TPD measurements are often utilized to provide the desorption characteristics. Since real-life samples are generated under ambient conditions, the potential for background effects is significantly enhanced. In many cases, background effects and their implications on data analysis are not considered. It will be demonstrated that background effects are very significant for real-life, field generated samples when traditional TPD measurements are performed. We have devised a novel experimental protocol to reduce background effects during TPD measurements of field generated, real-life, powdered samples. The novel experimental apparatus and procedures will be described. TPD spectra measured using the new protocol will be compared with spectra measured using traditional protocol.

MC-TuP22 A New Look at the Steel Cord-Rubber Adhesive Interphase by Chemical Depth Profiling*, **G.E. Hammer**,* The Goodyear Tire & Rubber Company

The adhesive interphase formed between brass plated steel cord and sulfur crosslinked rubber is known to be a complex layer of metal oxides, sulfides, and rubber. Hostile aging of this system produces changes in the structure, morphology, thickness and mechanical properties of this layer. In a previous publication it has been shown that the overall thickness of the sulfide layer as measured by depth profiling with Auger electron spectroscopy could be used to characterize the degradation of the adhesive bond.@footnote 1@ In this work multivariate statistical analysis of the sulfur Auger electron spectra was used to produce chemical depth profiles of the individual copper and zinc sulfide layers. These chemical depth profiles give new insight into the adhesion degradation mechanism on the nanometer scale. Particularly, the percentage of copper sulfide in the layer was found to be an accurate predictor of adhesion degradation. @FootnoteText@ @footnote 1@G. E. Hammer, R. M. Shemenski, J.Vac. Sci. Technol. A, 12(4), 2388 (1994).

MC-TuP23 Electrical Property of TiN@sub x@/SiO@sub 2@/Si Structure for Metal Gate Electrodes*, **K.S. Kim**, Y.C. Jang, K.J. Kim,* Sungkyunkwan University, South Korea*; N.-E. Lee, S. Youn, K. Roh, Y. Roh,* Sungkyunkwan University, South Korea, Korea

Recently, there have been growing research interests in the gate structures utilizing metal gate electrode materials including W in Si MOS devices. In order to avoid the strong interactions of F during W CVD with gate oxide layer leading to the destruction of gate oxide integrity, TiN@sub x@ diffusion barrier layer has been employed between the metal electrode and the gate oxide due to its excellent electrical property and structural stability. In this work, we investigated the interface formation between TiN@sub x@ and SiO@sub 2@ and electrical properties of TiN@sub x@/SiO@sub 2@ as a function of annealing temperature. Thermal gate oxide with the thickness of 110 Å was grown at 850 °C in the O@sub 2@ atmosphere by RTP on p-type Si. Then, TiN@sub x@ layers with the film thickness of 1000 Å were deposited at room-temperature by reactive d.c. magnetron sputtering with the Ar and N@sub 2@ gas mixture ratios of 6:1, 6:3, and 6:6. To minimize the radiation-induced damage of thermal gate oxide, plasma power was kept as low as 100 W during sputtering. Annealing of TiN@sub x@/SiO@sub 2@/Si structures was performed for 180 sec at 600, 700, and 800 °C by RTA in order to investigate the structural and chemical stability. AES and 4-point probe were performed to measure the chemical composition and sheet resistance (R@sub s@) of TiN@sub x@/SiO@sub 2@ films, respectively. The results of R@sub s@ measurements as a function of annealing temperature indicated that the R@sub s@ values of TiN@sub x@ films decreased at the annealing temperature below 600 °C but started to increase above 700 °C compared to those of as-deposited films. Increased R@sub s@ of the samples annealed at elevated temperature above 700 °C was attributed to the increased oxygen concentration in TiN@sub x@ layers, judged from the AES results. Microstructures of TiN@sub x@/SiO@sub 2@ interfaces investigated by cross-sectional TEM showed a good structural integrity.

MC-TuP24 The Observation of Ferroelectric Domains using Scanning Capacitance Microscope*, **M.K. Lee**,* Hyundai Electronic Industries Co. Ltd., Korea*; P. DeWolf, R. Alvis,* Digital Instruments, Veeco Metrology Group*; W.S. Yang, C.H. Lim, S. Heo, T.K. Lee, Y.B. Park, H.J. Kim, K.Y. Min, S.Y. Lee,* Hyundai Electronic Industries Co. Ltd., Korea

The ferroelectric domain structure affects the ferroelectric properties like as hysteresis loop characteristic that is of importance in manufacturing of ferroelectric random access memory (FeRAM). However, the domain images cannot be easily seen using a general analytic method. We have investigated the ferroelectric domain structure of SrBi@sub 2@Ta@sub 2@O@sub 9@ (SBT) using a scanning capacitance microscope (SCM) combined with an atomic force microscope (AFM). The ferroelectric domains were imaged by optimizing AC and DC bias between sample and cantilever tip. Integrating a dc/dv signal from single domain makes a microscopic ferroelectric hysteresis loop that corresponds well with a macroscopic one obtained from the same film. We also try to image the leakage current of SBT film by means of tunneling AFM (TunA). As the result, the weak point passing by the high currents was observed. Further study on the chemical composition or the structure of the weak point will be helpful to understand the leakage current mechanism of ferroelectric materials.

MC-TuP25 Improved Local Capacitance Detection and a Quantitative 1-D Carrier Profile Extracted from the Scanning Capacitance Microscopy dC/dV versus V Curves*, **E.-S. Kang**, J. Kang, H.-J. Hwang,* Chung-Ang University, Korea

We have quantitatively extracted 1-dimensional carrier profile from the scanning capacitance microscope (SCM) dC/dV versus V curves using the SCM modeling and an inversion modeling. This is based on the spherical capacitor model, not the common parallel-plate capacitor model. We physically analyzed the spherical capacitor and calculated the rate of capacitance change with bias. Our modeling data have resulted in the capacitance-voltage (C-V) curves different from the conventional C-V curves. The method for a quantitative carrier profiling can be applied directly th the 2- or 3-dimensional dopant profile extractions. Since the current SCM system has a poor reproducibility and sensibility for obtaining the local dC/dV curves, this problem will prevent us from acquiring carrier depth information. For a better quantity of the carrier profiling, for example, to obtain a carrier profile more than 10x18 cm@super -3@, we have designed a new capacitance detector operating at 1.8GHz voltage-controlled oscillator. It consists of an vco, a microstrip resonator, and a peak detector. It will bring a greater enhancement for the SCM sensitivity and performance.

MC-TuP26 Dynamic Force Microscopy Investigations on Molecular Structures and Electrical Properties of Organic Ultrathin Films*, **K. Kobayashi**, T. Fukuma, H. Yamada, T. Horiuchi, K. Matsushige,* Kyoto University, Japan

Dynamic force microscopy (DFM) was used to investigate the nanometer-scale structures and electrical properties of organic molecular films, which should be elucidated for their promising applications for molecular electronics. Frequency modulation (FM) detection method which can give high sensitivity especially in a vacuum environment was used in our DFM. The samples used in this study were organic ultrathin films such as self-assembled monolayers (SAMs) of alkanethiol molecules on Au(111) surface and fullerene crystalline islands deposited on Si(111) surface. On fullerene crystalline islands, we successfully obtained molecularly-resolved images, in which molecules were hexagonally packed. Local variation in surface potential (SP) was also mapped using Kelvin null method in DFM, which allowed us to study the local charge transfer between fullerene thin films and the substrate. In the SP image, a small contact potential difference (CPD) between the fullerene crystalline islands and monolayer-covered Si(111) surface was measured. In addition, we obtained molecularly-resolved images on both SAMs of short-chain alkanethiol molecule (octanethiol) and long-chain molecule (hexadecanethiol). The fact that the latter long-chain SAMs could not be imaged by scanning tunneling microscopy (STM) due to the poor electrical conductivity demonstrates a remarkable advantage of DFM for the studies of organic thin films.

MC-TuP27 Conservative and Dissipative Tip-sample Interaction Forces Reconstructed from Dynamic Atomic Force Microscopy Data*, **B. Gotsmann**, H. Fuchs,* University of Muenster, Germany

The conservative and dissipative forces between a tip and a surface are characteristic for the materials involved and contain information on several material parameters. In order to determine these forces quantitatively at all tip-sample distances dynamic atomic force microscopy (AFM) can be used. We based our analysis on a combination of computer simulations and experimental AFM data obtained by the frequency modulation technique. In this way it became possible to reconstruct complete force versus distance curves and damping coefficient versus distance curves from experimental data (frequency shift and energy dissipation) without using free parameters and without using a predefined model for the interaction.@footnote 1@ As an example the interaction between an Al-tip and a Au(111)-sample under UHV conditions was analyzed. It turned out that the parts of the force curves that correspond to long range van-der-Waals-forces as well as strong repulsive contacts can be described well with known contact models. However in the transition regime between attractive and repulsive contact an additional short range force can be found. Similarly, the friction coefficient can be determined quantitatively up to a distance of several nanometers exhibiting an inverse power law. At closer contact both velocity dependent friction and adhesion hysteresis lead to energy dissipation. A strategy to distinguish between the two in AFM experiments will be discussed briefly. @FootnoteText@ @footnote 1@ B. Gotsmann, C. Seidel, B. Anczykowski, H. Fuchs, Phys. Rev. B 60 (1999) p.11051.

MC-TuP28 Challenges in Insulator Surface Analysis*, **M. Reichling**, C. Barth,* Universit@um a@t M@um u@nchen, Germany*; M. Huisinga, R. Lindner,* FU Berlin, Germany

The application of high end ultraviolet optical materials as required for next generation optical lithography is extremely demanding in terms of preparing defect free surfaces. We report about major progress in insulator surface analysis with respect to both, characterizing the electronic and geometric surface structure. This is exemplified for crystals with the fluorite structure (CaF@sub 2@, SrF@sub 2@, BaF@sub 2@) that are important materials for advanced ultraviolet optical applications. Results from highest sensitivity ultraviolet photoelectron spectroscopy revealing defect states are presented. Supported by additional evidence from ultrafast laser spectroscopy, we demonstrate that for any preparation there are occupied and unoccupied states throughout the band gap where the density of states strongly decreases with energy above the valence band edge. The sources of the band gap states as well as their implications for optical absorption in the ultraviolet are discussed. We recently presented atomic resolution in imaging defects on a fluoride surface with scanning force microscopy in the ultra-high vacuum.@footnote 1@ With such measurements and controlled gas exposure we can show that chemical interactions between gas molecules and surface defects play a major role in the degradation of surfaces exposed to air. We, furthermore, demonstrate that it is now possible to resolve not only defects on terraces of cleaved surfaces but also features like step edges and kinks with atomic resolution and that we are able to locate positions of individual ions and vacancies along steps. We present recent results where we resolved individual atoms in regular nanometer-sized surface clusters that are a result of cleavage. @FootnoteText@ @footnote 1@ M. Reichling, C. Barth, Scanning force imaging of atomic size defects on the CaF@sub 2@(111) surface, Phys. Rev. Lett. 83(4), 768 (1999).

MC-TuP29 Controlled Surface Charging as an Analysis Tool in XPS of Mesoscopic Systems*, **H. Cohen**, K. Shabtai, S.R. Cohen, I. Rubinstein,* Weizmann Institute of Science, Israel

A novel application of X-ray photoelectron spectroscopy (XPS) is presented, using controlled surface charging (CSC) in dielectric/conductive mesoscopic heterostructures. The method is based on the induction of well-defined potential gradients by means of the electron flood gun. The resultant local potential variations are projected on the photoelectron energy scale, directly detected as XPS line shifts, providing high-quality spatial information down to nanometer scale resolution. The method is applicable to a large variety of systems, offering important advantages over existing XPS-based techniques. Applications of the method will be demonstrated.

Magnetic Interfaces and Nanostructures
Room Exhibit Hall C & D - Session MI-TuP

Poster Session

MI-TuP1 Magnetic Properties of Ultrathin Co Films on Si(111)*, H. Xu,* National University of Singapore, Singapore*; A. Wee, A. Huan,* National University of Singapore

The growth and magnetic behaviour of ultrathin cobalt films on clean(7x7) and Au covered Si(111) were investigated. All experiments including molecular beam epitaxy (MBE) were performed in an ultra-high vacuum (UHV) chamber with a background pressure of 5x10@super-11@ mbar. The Si substrates were introduced via a load-lock and firstly outgassed over night, then the substrates were further cleaned by flashing to 1500K by resistive heating for several seconds. The UHV system was equipped with Auger electron spectroscopy (AES), scanning tunneling microscopy (STM), low energy electron diffraction (LEED) and magneto-optic Kerr effect (MOKE). The growth process was studied using STM and LEED. Magnetic properties were determined with MOKE. It was found that Co nucleates in the initial stage that prefer to grow along the bunched step-edges of the Si substrate(), which leads to a strong in-plane uniaxial anisotropy (hard axis along<-110> direction). By introducing Au buffer layers, the tendency for step decoration is reduced, Co grains begin to coalesce on the terrace, so that in-plane uniaxial anisotropy is reduced. However, the magnetic characteristics were improved by the deposition of a Au buffer layer, which partially blocks the silicide reaction between Si and Co. The ferromagnetic inactive layer was found to be decreased to 2.2 ML. By using an higher flashing current, unbunched steps are created on same Si substrate. It is suggested that in this way much more regions for reaction between Si and Co grains arise and a larger amount of CoSi@sub2@ is formed which then deteriorate the magnetic properties of the film in initial layers. Furthermore, in terms of Néel domain wall model and microstructure, different dependencies of coercivity vs. film thickness were discussed.

MI-TuP2 Model Based Design of Next Generation Ion Beam Deposition Systems*, H.N.G. Wadley,* *W. Zou,* University of Virginia, usa*; X.W. Zhou, J.J. Quan, Y. Sun, S. Subha,* University of Virginia*; T. Hylton, G. Hufnagel,* CVC Commonwealth, Inc.

Ion beam deposition (IBD) is increasingly used for the growth of giant magnetoresistive (GMR) multilayers and magnetic tunnel junction (MTJ) devices. The performance of both device types is a very sensitive function of the layer thickness, the metal atom deposition rate, incident angle and energy, together with the reflected neutral flux and energy at the substrate. These in turn depend upon the ion gun, target, substrate geometry, the ion gun voltage, the ion type, the extent of target dither and substrate rotation, the background pressure, and any shaping of the metal flux. Optimally selecting these parameters for the three or more metal targets in the deposition system has become very challenging to IBD tool designers. A Multiscale model has been used to simulate the Ion Assisted Ion Beam Deposition of GMR structure. The model allows the thickness of a metal layer and the metal atom incident angle over the surface of a wafer to be optimized by selection of the ion type and energy, target placement, orientation and dither, substrate placement and rotation, and background pressure. A molecular dynamics approach based on embedded atom method potentials is used to investigate the effects of process parameters such as assisting ion energy on the interfacial roughness and the interlayer mixing during the deposition of giant magnetoresistive (GMR) multilayers. The atomic scale mechanisms of mixing and roughening at the various interfaces are identified. This simulation can then be used to identify improved deposition systems that can meet the film thickness uniformity, interface morphology and atomic scale structure, target needed for the high yield manufacture of GMR devices.

MI-TuP3 Preparation of Cross-sectional TEM Specimens of Obliquely Deposited Magnetic Thin Films on a Flexible Tape*, E.G. Keim,* *M.D. Bijker, J.C. Lodder,* University of Twente, The Netherlands

Specimen preparation is an essential part of Transmission Electron Microscopy (TEM). In general, if one is interested in interface and/or film properties one should prepare a TEM specimen in cross-section. Upon surveying the literature, no recipe is provided for the preparation of TEM cross-sections of Metal Sputtered (MS) or Metal Evaporated (ME) magnetic thin films on polymer substrates. Various private communications in the field@footnote 1,2@ reinforce our impression that no adequate preparation procedure for this class of materials is available at present, although proper quality TEM images of ME tapes in cross-section have been published previously@footnote 3-9@ without an adequate description of TEM specimen preparation though. TEM cross-sections of MS or ME tapes pose several unique problems during preparation. In this paper we will present a recipe for making cross-sectional TEM specimens which is especially benificial for brittle metal layers even on polymer base films, resulting in large homogeneous electron transparent areas and leaving the very fragile polymer tape substrate and glue layer completely intact. Our recipe proves to be a good alternative to the use of a microtome. Apart from the sample preparation method also some details of the deposition technique will be elucidated. @FootnoteText@ @footnote 1@ J. Jodge and Peng Tang, Private communication (1999), Quantum Corp., USA.,@footnote 2@ H. te Lintelo, Private communication (1999), IST Corp., Belgium.,@footnote 3@ S. Honodera, H. Kondo, and T. Kawana, MRS Bulletin. 21(9), 35 (1996).,@footnote 4@ H. Ho, G. Gau, and G. Thomas, J. of Appl. Phys. 65(8) , 3161 (1989).,@footnote 5@ K. Sato, K. Chiba, T. Ito, T. Ssaki, and J. Hokkyo, J. of Appl. Phys. 69(8), 4736 (1991).,@footnote 6@ J. Hokkyo, T. Suzuki, K. Chiba, K. Sato, Y. Arisaka, T. Sasaki, and Y. Ebine, JMMM 120, 281 (1993).,@footnote 7@ P. ten Berge, L. Abelmann, J. C. Lodder, A. Schrader, and S. Luitjens., J. of The Magnetics Society of Japan 18(S1), 295 (1994).,@footnote 8@ M.D. Bijker, E.M. Visser, and J.C. Lodder, Tribology International 31(9), 553 (1998).,@footnote 9@ H.J. Richter, IEEE Transactions on Magnetics 29(1), 21 (1993).

MI-TuP4 Magnetic Transition at the Gd(0001) Surface*, C.S. Arnold,* *D.P. Pappas,* National Institute of Standards and Technology, Boulder

Controversy surrounds the magnetic ordering properties of the Gd(0001) surface. Several reports conclude that the surface has an it\{extraordinary} transition, ordering at a Curie temperature significantly higher than that of the bulk, while others reports have failed to reproduce this result. Our experiments unambiguously prove that the Gd(0001) surface has an ordinary transition. Furthermore, by analyzing both the bulk and surface magnetization, we show that Gd(0001) films are good realizations of semi-infinite, 3-dimensional Heisenberg ferromagnets with identical exchange couplings for surface and bulk, and identical Curie temperatures.

Nanotubes - Science and Applications
Room Exhibit Hall C & D - Session NM-TuP

Poster Session

NM-TuP1 Growth and Purification Characteristics of Isolated and Aligned Carbon Nanotubes*, M. Kang,* *K. Ryu, Y.C. Kim,* Hanyang University, Korea*; H. Jeon,* Hanyang University, Korea, South Korea

Carbon nanotubes of the interesting applications is reported for display application, but neither industrial fabrication technology nor performance has been reported for practical display application. Therefore, we studied that carbon nanotubes (CNTs) were grown on nickel deposited glass substrates at low temperature (about 650°C) by plasma enhanced chemical vapor deposition (PECVD) method using a mixture of CH@sub 4@, NH@sub 3@, and H@sub 2@ gaseous sources. CH@sub 4@and H@sub 2@ were used as main reactant gases, and NH@sub 3@ was used as both dilution and nickel layer pretreatment source. Nickel layer with a thickness of several hundreds nm was deposited using ultra high vacuum (UHV) e-beam evaporator and pretreated with NH@sub 3@ plasma to form isolated nano size nickel island before CNTs deposition. Nickel catalyst thickness and NH@sub 3@ plasma treatment significantly affected CNTs microstructure and alignment. CNTs size was generally increased with increasing nickel thickness. Aligned@footnote 1,2@ and isolated CNTs with a typical dimension of a few hundreds nm in diameter and several @micro@m in length were observed. Post hydrogen and oxygen plasma treatments successfully eliminated carboneous impurities and nickel caps on CNTs. In this presentation, a comprehensive understanding of the effect of NH@sub 3@ plasma treatment on nickel catalyst layer and plasma purification processing will be described. We examined the properties of carbon nanotubes by SEM, XRD, Raman spectroscopy and TEM. @FootnoteText@ @footnote 1@ Synthetic Metals 108(2000) 159-163 @footnote 2@ Appl.Phys.Lett., Vol.75, No.8, 23 .

NM-TuP2 Selective Area Growth of Carbon Nanotubes on Glass Substrate*, J.B. Yoo,* *J.H. Han, H.J. Kim, W.S. Yang, J.H. Yang, C.Y. Park,* Sungkyunkwan University, Korea

Carbon nanotubes have received considerable attention because of their own unique physical properties and many of potential applications. Selective area growth of carbon nanotubes is very important for the electronic device applications such as FED, TubeFET, SET, interconnects, sensor etc. In this study, selective area growth of vertically aligned carbon nanotubes was performed on nickel-coated glass and silicon (100) with and without buffer layer at temperatures below 600°C by hot filament plasma enhanced chemical vapor deposition (HFPECVD). The effects of growth parameters on the growth and emission characteristics of carbon nanotubes were investigated and compared to planar growth. Growth mechanism of selective area growth was proposed. The morphology of nanotubes was examined by field emission scanning electron microscopy (FESEM), and the microstructure of selective area growth of carbon nanotubes was investigated by high resolution transmission electron microscopy (HRTEM).

NM-TuP3 Effects of Metal-Catalyst and Buffer Layer on Growth and Emission Properties of Carbon Nanotubes*, **J.H. Han**, H.J. Kim, W.S. Yang, J.B. Yoo, J.H. Yang, C.Y. Park,* Sungkyunkwan University, Korea*; Y.H. Song, K.S. Nam,* ETRI, Korea

Carbon nanotubes have been extensively studied because of their own unique physical properties and their potential applications such as flat panel displays and vacuum microelectronics. In practical applications, roles of metal-catalyst and buffer layer, particularly, are very important to growth and adhesion of carbon nanotubes respectively. Therefore, a systematic study for metal-catalyst and buffer layer has been so indispensable. In our experiments, we have used buffer layer such as chrome or molybdenum or titanium to improve the adhesion between metal-catalyst layer (such as nickel, cobalt, and nickel-cobalt composite) and glass substrate. We have grown the vertically aligned carbon nanotube arrays on nickel-coated glass and silicon (100) with adhesive buffer layer at temperatures below 600°C by plasma enhanced chemical vapor deposition (PECVD). In this work, a dc plasma was employed, and acetylene gas was used as a carbon source and ammonia gas was used as a catalyst and dilution gas. We examined the effect of thickness of metal-catalyst and buffer layer on the growth and emission properties of carbon nanotubes. The emission characteristics of nanotubes were evaluated in vacuum chamber using phosphor-coated anode. The morphology of nanotubes was examined by field emission scanning electron microscopy (FESEM), and the microstructures of interface between metal-catalyst and buffer layer or buffer layer and glass (or silicon) were investigated by high resolution transmission electron microscopy (HRTEM).

NM-TuP4 Emission Properties of Field Emission Triode using Carbon Nanotubes Grown on Glass Substrate*, **H.J. Kim**, J.H. Han, W.S. Yang, J.B. Yoo, Y.W. Jin, J.E. Jung, J.H. Yang, C.Y. Park,* Sungkyunkwan University, Korea*; N.S. Lee, J.M. Kim,* Samsung Advanced Institute of Technology, Korea

Carbon nanotubes are potential candidates for cold cathode field emitter because of high aspect ratio and small radii of curvature at their tips with high chemical stability, thermal conductivity, and mechanical strength. The vertical alignment of carbon nanotubes in large area is important to FED application. We have fabricated the triode for field emission display using carbon nanotube as an emission tip. First, 1.2 @micro@m thick SiN@sub x@ as an insulator was deposited on the Ni coated glass substrate with Cr buffer layer by PECVD, and 100nm thick Mo as a gate electrode was deposited by DC sputter. Carbon nanotubes were directly grown on substrate using selective area growth technique after gate opening and insulator etching using conventional lithography process. Vertically well-aligned multiwall carbon nanotubes weres grown by PEHFCVD(Plasma Enhanced Hot Filament Chemical Vapor Deposition). The carbon nanotubes were about 40nm in diameter. The emission characteristics of the fabricated carbon nanotube triode shows very low operating voltage compared to that of conventional Spindt-type FEDs. The uniformity of emission characteristics of nanotubes were evaluated in vacuum chamber using phosphor-coated anode. The morphology of nanotubes was examined by field emission scanning electron microscopy (FESEM).

Photonics

Room Exhibit Hall C & D - Session PH-TuP

Poster Session

PH-TuP1 Optical Processes in PMMA, SiO@sub 2@ and Hybrid Organic-Inorganic Sol-Gel Films Colored with Rhodamines*, **J.J. Pérez-Bueno**, S.R. Vazquez-García,* Universidad Autónoma de Querétaro, México*; L. García-González,* Unidad Querétaro, México*; Yu.V. Vorobiev, J. González-Hernández,* Unidad Querétaro, México, Mexico

Various types of rhodamines (B-500, 6GDN), at different concentration, have been introduced in thin layers formed by a single matrix (SiO@sub 2@ or PMMA) and by a hybrid matrix, that is, a mixture of SiO@sub 2@ and an acrylic polymer, at variuos proportions. Firts, the precursor acrylic polymer was synthesized using the following components: 2-hydroxyethyl methacrylate (37.3 %), butyl acrylate (36.3 %), styreno (20.0 %), methyl methacrylate (4.4 %) and isobutyl methacrylate (2.0 %). Before solidification, the precursor avrylic polymer was dissolved in a mixture of 2-propanol and 2-butoxyethanol and then the tetraethyl-orthosilicate (TEOS) added to that solution. The hydrolisation and polycondensation were catalyzed using HCl. The optical absorption and the photoluminescence of layers on glass substrates were measured. It is found that the spectral position and fine structure of rhodamine absorption band greatly depend on the type of matrix. The luminescence intensity in layers with the PMMA and hybrid matrix is more intense than that of the layers with the SiO@sub 2@ matrix. The effects produced by the aggregation of the rhodamin molecules and their local environment on the optical processes addressed above are discussed.

PH-TuP2 Band Gap Modulation from 0.5 eV to 1.5 eV Employing the Alloy (CdTe)@sub x@(In@sub 2@Te@sub 3@)@sub 1-x@@footnote 1@*, **M. Meléndez-Lira**,* CINVESTAV-IPN, México*; M. Zapata-Torres,* CICATA-IPN, México*; R. Castro-Rodríguez,* CINVESTAV-IPN, México

CdTe is a semiconductor with a wide range of applications and alloyed with S, Zn, or Se allows high energy band gap modulation. To increase the range of band gap modulation in the near infrared employing CdTe alloys is a very interesting possibility with potential applications in the optoelectronic industry. We produced thin films of the alloy (CdTe)@sub x@(In@sub 2@Te@sub 3@)@sub 1-x@ employing the close spaced vapor transport technique combined with free evaporation. As sources we employed CdTe and In@sub 2@Te@sub 3@ powders. Composition was controlled by the temperature of sources and substrate. Structural characterization was carried out employing X-ray diffraction, scanning electron microscopy and atomic force microscopy. Chemical composition was determined by energy dispersive X-ray analysis. Room temperature transmission and photoreflectance spectroscopies were employed for optical characterization. The results shown that for single phase samples a sharp transition band edge in the transmission spectrum is obtained. From it a potential band gap modulation in the range from 0.5 eV to 1.5 eV is clearly observed. Photoreflectance results clearly showed that the band edge is of the direct type. The feasibility of the alloy is discussed taking in account the higher solubility of CdTe in In@sub 2@Te@sub 3@ because of its ordered vacancy structure. The band gap change is correlated with the indium content in the samples. @FootnoteText@@footnote 1@ Work partially supported by CONACyT.

PH-TuP3 Waveguiding in Microchip Lasers*, **N.J. van Druten**,* Leiden University and Delft Technical University, The Netherlands*; S.S.R. Oemrawsingh, Y. Lien, C. Serrat, M.P. van Exter, J.P. Woerdman,* Leiden University, The Netherlands

Microchip lasers@footnote 1@ typically consist of a thin, rare-earth-doped laser crystal, dielectrically coated on both surfaces to form a complete optical cavity. They are small and can be manufactured cheaply, because only a small amount of material is needed. Transverse-mode formation in microchip lasers is of considerable complexity, because it is the result of several competing waveguiding mechanisms, such as (i) the weak curvature of the mirrors, (ii) thermal lensing, and (iii) gain guiding (including gain-related index-guiding). The latter two depend critically on the material properties of the laser crystal. We have made a careful experimental and theoretical@footnote 2@ study of the transverse-mode formation in microchip lasers, in particular combining (i) and (iii), and concentrating on the regime where these two guiding effects have similar strength. The experiments were performed on a Nd:YVO@sub 4@ microchip laser with a plano-concave cavity configuration, longitudinally pumped by a transversely Gaussian pump beam derived from a titanium:sapphire laser. A surprisingly varied collection of mode profiles was found, deviating significantly from the standard Laguerre-Gaussian modes that are usually found for such cylindrically symmetric cases. In addition, the far-field profiles were generally found to be considerably different from the near-field profiles. We have also found cases where the far-field pattern has a minimum on axis (i.e., conical emission), while the near-field profile has an on-axis maximum. The agreement between theory and experiment is excellent, in particular when one considers the large variations in the observed mode profiles and the relative simplicity of our theoretical model. @FootnoteText@ @footnote 1@ J. J. Zayhowski and A. Mooradian, Opt. Lett. 14, 24 (1989). @footnote 2@ C. Serrat, M. P. van Exter, N. J. van Druten, and J. P. Woerdman, IEEE J. Quant. Electron. 35, 1314 (1999).

**PH-TuP4 Integrated Optoelectronic Sensor Based on GaN*, D. Starikov,* *E. Kim, C. Boney, J.-W. Um, I. Hernandez, N. Medelci, A. Bensaoula,* University of Houston

An integrated optoelectronic sensor based on GaN grown on sapphire by RF-assisted MBE is presented. The sensor combines inter-digitated line arrays of light emitting diodes (LEDs) and photodiodes based on Schottky barriers and fabricated in a single technological process. Under reverse bias the LEDs exhibit broad-spectrum avalanche emission with a strong band in the range from 365 to 475 nm. At forward bias the LED emission is more intense and forms a band from 400 to 600 nm. The photodiodes are sensitive in a spectral range from at least 250 to 400 nm. In the absorption/reflection mode the sensor operation is based on the spectral match between the avalanche emission and the photodiode sensitivity in the range from 365 to 400 nm. Using this set up, Acridine concentration measurements in aqueous solutions were performed using the absorption band of 300-450 nm. The fluorescence measurements were based on detection of the delayed fluorescence emission measured from alcohol solutions of Fluoran dye in the range from 290 to 320 nm under excitation with short optical pulses from the LEDs. The working range and the sensitivity of the sensor were evaluated using preset calibrated concentrations and will be presented during the presentation. This work was funded by Institute of Space Systems and Operations, NASA, and Texas ATP. The material is based in part upon work supported by the Texas Space Grant Consortium.

PH-TuP5 Fabrication and Optical Properties of Ordered Nanoscale Silicon Structures*, A. Wellner,* *R. Neuendorf, R.E. Palmer,* The University of Birmingham, UK

Reactive ion etching (RIE) of Silicon wafers using predeposited metal clusters (Ag, Au, Ni) as nanoscale etch masks yields Silicon nanopillars with extremely high aspect ratios @footnote 1,2@ The size of the individual pillars, their separation and their arrangement is mainly determined by the method used for cluster deposition. The cluster deposition can be varied between the two extreme conditions of i) random cluster deposition, resulting in randomly arranged pillars of lateral dimensions reflecting the cluster size distribution or ii) deposition of size selected clusters through a template consisting of a self-assembled monolayer of nanometer-sized polymer balls, resulting in well ordered arrays of nearly equal size pillars. In this work we investigate the structural and optical properties of ordered and dis-ordered 2D arrangements of Silicon pillars through a combination of Scanning Electron Microscopy (SEM) with optical spectroscopy methods such as absorption/ reflection spectroscopy and photoluminescence spectroscopy (PL). Ordered pillar arrays show evidence of a developing photonic band gap in good agreement with theoretical predictions using the generalized Mie theory (GMT), while systems with pillar diameters (15nm exhibit exciton features characteristic of quantum confinement. @FootnoteText@@footnote 1@K. Seeger and R. E. Palmer, Appl. Phys. Lett. 74, 1627 (1999) @footnote 2@K. Seeger and R. E. Palmer, J. Phys. D 32, L129 (1999).

PH-TuP6 Etching of Optical Coating Oxides in Fluorine and Chlorine Plasmas*, W.B. Song,* *W. Liu, J.J. Talghader,* University of Minnesota

With the increasing use of micro-optical components in optoelectronics and MEMS, it is becoming increasingly important to understand the behavior of traditional optical materials in the microfabrication environment. For this purpose, we studied the etching of optical coating oxides in a variety of fluorine and chlorine plasmas. The oxides used in this study are Al@sub 2@O@sub 3@, HfO@sub 2@, Nb@sub 2@O@sub 5@, SiO@sub 2@, Ta@sub 2@O@sub 5@, TiO@sub 2@, Y@sub 2@O@sub 3@, and ZrO@sub 2@. These coatings are transparent from the near IR to UV and have a broad range of refractive indices. Using the well-known etching chemistry of SiO@sub 2@ as a guide, we attempt to correlate the volatility of the etch products of these oxides to the observed etching behavior in CF@sub 4@, SF@sub 6@, Cl@sub 2@, and their derivatives such as CF@sub 4@+O@sub 2@, etc. The results show that the volatility predicts general etch reactions with good accuracy, but is less successful in predicting relative etch rates. For example, our results show that Nb@sub 2@O@sub 5@, Ta@sub 2@O@sub 5@, TiO@sub 2@ and SiO@sub 2@ are etched in fluorine plasmas, while Al@sub 2@O@sub 3@, HfO@sub 2@, Y@sub 2@O@sub 3@, and ZrO@sub 2@ are not. All of the etched oxides have fluorine compounds with melting or sublimating temperatures less than 300°C. Increasing the substrate temperature to 340°C does not affect the behavior of the unattacked oxides. In chlorine plasmas, all of the oxides show some nonzero etch rate, which also matches with published volatility data. Finally, we present the selectivity of the oxides based on the obtained results.

PH-TuP7 Study of the GaAs etching with the Electron Cyclotron Resonance Source Plasmas*, P. Kumar,* *S.K. Angra, L.M. Bharadwaj, R.P. Bajpai,* Central Scientific Instruments Organisation, India

The III-V materials are precisely used for the fabrication of the Optoelectonics devices as LEDs, laser diodes and high speed electronics devices. The devices fabrication process in the line is mainly used 13.56 MHz RIE system with the different gases combinations such as BCl@sub3@,Cl@sub2@ , hydro carbon and further activated them using the Ar ions into it. The reactive ion beam etching combined with the Electron Cyclotron Resonance discharge plasma (ECR-RIBE) and chemically assisted ECR plasma etching is especially useful , because of its highly directional and causes low damage. In this article, we had investigated the of GaAs etching using the Electron Cyclotron Resonance Cl@sub2@ plasma operated at 2.45 GHZ. Also the first time the Chemically assisted ECR plasma etching of the GaAs was investigated with the combination of the Ar/I@sub2@. The optimization of the system for the etching of GaAs was carried out with the numerous different parameters such as flow rates of the gases such as chlorine and added up Ar into cholrine, bias to the stage or substrate in the range of 15to 100 volt dc bias, partial pressure ranging from 0.1 mTorr to 1 mTorr of the process chamber, variation of the space between stage to the exit windows of the plasma source and measurements of uniformity of process over the 2 to 6 inches were studies. The Argon plasma is exposed to the substrate while Iodine is directly implemented to the substrate for the chemically assisted process. The results are qualitatively put into accordance with the observed reactive species of the plasma using the optical emission spectroscopy and also with the total plasma density calculated using Langmuir probe measurements of the plasmas. The etching uniformity of the substrate of 2, 3, 4 and 6 inches was performed and that is matched with the plasma ion density uniformity measurements and attempts were put forward to improve the uniformity by further confinement of the plasma using the magnetic field and also putting the biasing to the substrate.

PH-TuP8 Effect of Dry Etching Conditions on Surface Morphology and Optical Properties of GaN Films in Chlorine-Based Inductively Coupled Plasmas*, Y.B. Hahn,* Chonbuk National University, South Korea*; B.-C. Cho,* LG Precision Co., Ltd.*; Y.-H. Im,* Chonbuk National University, South Korea

A parametric study on dry etching of undoped, n- and p-type GaN films has been carried out in a planar type inductively coupled plasma (ICP) system. The effect of etching conditions on surface chemistry, morphology, and optical properties of GaN Films etched in Cl2/Ar discharges was studied in detail using atomic force microscopy (AFM), scanning electron microscope (SEM), and photoluminescence (PL) measurement. The GaN films showed overall similar etching characteristics. Although the surface roughness was dependent on plasma parameters, it was a strong function of dc bias voltage. The surface roughness was relatively independent of the rf power up to 150 W, resulting quite smooth morphology (rms roughness 1.1 - 1.3 nm), while etching at higher chuck powers (> 200 W) produced rougher surface due to increased ion bombardment. Stoichiometry at the etched surface of undoped and p-type GaN films was maintained, indicating equirate removal of component. By contrast n-GaN showed some depletion of nitrogen from the surface. The lattice disorder and point defects were much less generated during the ICP etching than reactive ion etching (RIE). The PL peak of etched p-GaN was somewhat red-shifted from 366 nm to 460 nm, but it showed a strong peak intensity after ICP etching, which was very similar to the result obtained after thermal annealing of as-grown p-GaN films.

PH-TuP9 Plasma Etching Research in Integrated Photonics*, K.H.A. Bogart,* *M.A. Cappuzzo, L.T. Gomez, J.F. Bailey, R.W. Long,* Bell Laboratories, Lucent Technologies

The skyrocketing consumer demand for greater Internet access, telecommunications, and other broadband services has accelerated the need for advanced lightwave transmission capacity such as wavelength division multiplexing (WDM). WDM transport is evolving into dynamic WDM systems requiring several optical components including sources, waveguide grating routers, reconfigurable add/drops, optical amplifiers, and optical cross connects. Integration of these components is vital for decreasing fiber insertion losses and for low cost manufacturing and packaging. Silicon optical bench (SiOB) technology leverages off the mature silicon integrated circuit (IC) industry by utilizing photolithography, thin film deposition and etching techniques to create complex planar optical devices on the silicon platform. In contrast to IC's, SiOB devices are several micrometers to centimeters in length and use optical quality materials, thus producing diverse challenges in materials processing. Plasma etching of planar waveguide devices such as waveguide routers, amplifiers, optical compensators, and switches will be examined with a focus on newer high-delta optical materials such as Ge- or Ti-doped silica (delta = refractive index difference between the waveguide core and the surrounding cladding), aluminosilicates, and ferroelectric materials. Comparisons of photoresist and hardmask materials such as poly-silicon and aluminum oxide will be made. Potential solutions to integration issues with the high-delta materials will also be presented.

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

PS-TuP1 Frequency Effects to E - H Discharge Mode Transitions in Inductively Coupled Plasmas*, M. Edamura,* Hitachi, Ltd., Japan*; E. Benck,* National Institute of Standards and Technology

Inductively coupled plasmas (ICPs) have been used for plasma processes because of their high density and low pressure operation. Recently relatively lower density plasmas are used for many etching processes because the newest semiconductor devices have very small structures. Especially when ICP etching reactors are driven at low power, the effect of E-discharge (capacitive coupled discharge) can not be neglected. There are a wide variety of ICP reactors and the characteristics of E-discharge strongly depends on the reactor design. In this work, frequency effects to ICPs and E - H discharge mode transitions in ICPs are examined by Langmuir probe measurement. An ICP modified GEC reference cell and the discharge frequencies of 6.28 MHz, 13.56 MHz and 20.0 MHz were used for the experiment. By increasing discharge power, plasmas jump to high density H-mode discharges from low density E-mode discharges at certain powers. Higher frequency makes the voltage of the coil and the E-mode density higher and thus the E-H mode transitions occur at lower power. On the other hand, higher frequency makes the density of H mode lower because contribution of E-discharge in H mode makes the efficiency of plasma generation lower. Electron energy distribution functions (EEDFs) of 20 MHz discharge shows a high energy tail around 7-15 eV caused by the E-discharge between the coil and the plasma. Once the E-discharge contribution was removed by inserting an electrostatic shield, significant difference of EEDFs was not observed at these three frequencies.

PS-TuP2 Effect of Wafer Temperature on High Aspect Ratio Hardmask Etching*, S. Lee,* *Y.C. Tien, Y.D. Chang,* Winbond Electronics Corporation, Taiwan

Fluorocarbon-based chemistries were used to study the effect of wafer temperature on the etch of high aspect ratio hardmask composed of BSG and Si@sub 3@N@sub 4@ layers. It is found that etch stop can occur easily at high temperature. The rate of polymer deposition plays an important role in etch stop. The etching rates were found to be inversely proportional to the wafer temperature. Such a relation indicates a negative activation energy in hardmask etching using fluorocarbon plasma. It also implies that in hardmask etching, complicated gas-surface reactions, but not simple one-step reaction, are involved. Different wafer surface temperature can provide different degree of activation for etching reactions. It is also observed that etching rates are very sensitive to the chamber condition, as indicated by optical emission spectroscopy. Analysis of etching rate and emission intensity trends indicates that CF@sub x@ may contribute more than F does in the etch of BSG and Si@sub 3@N@sub 4@, since polymer-rich etching chemistries were used. Reaction models are proposed to interpret the observed trends.

PS-TuP3 Time Resolved Mass Spectrometric Plasma Diagnostics*, G.J. Peter,* *G. Nicolussi,* Balzers Instruments, Liechtenstein*; N. Mueller,* Balzers Instruments, Liechtenstein, Principality of Liechtenstein

The energy distribution of the ions in a plasma is one of the most important process parameters. This distribution can be measured for different ion species by a combination of an electrostatic energy filter and a mass spectrometer (a Plasma Process Monitor PPM). Thus far, most of such investigations have been performed in plasmas under equilibrium conditions. On the other hand, little is known about the ion energy distribution during ignition of plasmas, i.e. in a non-equilibrium state. Furthermore, it has become a common technique to modulate deposition and cleaning plasmas by means of periodically changing magnetic and/or electric fields which as well results in non-equilibrium plasma conditions. Measurements of the transient ion energy distributions in such processes contribute to a deeper understanding of the mechanisms involved. This in turn, facilitates process development in order to avoid conditions that might result in electronic device damage (e.g. due to high energetic ions). Our investigation includes 3 different non-equilibrium plasmas: A DC-planar magnetron plasma during ignition, a magnetically modulated DC plasma, and a power modulated RF-plasma. The PPM utilized in these experiments is a combination of a differentially pumped specially adapted cylindrical mirror energy analyser and a quadrupole mass filter with mass ranges from 0 - 512 amu up to 0 - 2048 amu. An energy resolution of 0.3 eV and unit mass resolution over the whole mass range are achieved. To perform time resolved measurements the mass and energy filter are set to the desired values and data acquisition is made with a Multi-Channel Scaler (MCS).

PS-TuP4 The Boron Effects on YMnO@sub 3@ Thin Films Etching in High Density Ar/Cl@sub 2@/BCl@sub 3@ Plasma*, B.J. Min,* Chungang University, Korea*; Y.T. Kim,* KIST, Korea*; C.-I. Kim,* Chungang University, Korea

Ferroelectric materials, such as Pb(Zr,Ti)O@sub 3@ (PZT), SrBi@sub 2@Ta@sub 2@O@sub 9@ (SBT), (Ba,Sr)TiO@sub 3@ (BST), YMnO@sub 3@ have attracted much attention for use in nonvolatile memories. In particular, YMnO@sub 3@ thin films are excellent materials for high integrated ferroelectric random access memory (FRAM) with metal-ferroelectric-silicon field effect transistor (MFSFET) structure. Although etching processes for YMnO@sub 3@ thin films must be developed to fabricate MFSFET type FRAM, etching of YMnO@sub 3@ have not been reported. Thus, we studied the etching properties of YMnO@sub 3@ thin films using high density plasma. In this study, YMnO@sub 3@ thin films were etched with Ar/Cl@sub 2@/BCl@sub 3@ gas chemistries in inductively coupled plasma (ICP). Photoresist (PR) and SiO@sub 2@ were used as mask materials. Etching properties of YMnO@sub 3@ were measured according to the various etching parameters such as rf power, dc bias voltage, chamber pressure and gas mixing ratio. The trends in the effect on etch rate and selectivity to mask materials for BCl@sub 3@ ratio to Ar/Cl@sub 2@ have been determined. YMnO@sub 3@ was dominantly etched by Ar ion bombardment. Selectivity to PR and SiO@sub 2@ increased as decreasing mole fraction of Ar gas. Additive BCl@sub 3@ enhanced relative etch rate, selectivity and profile. Chemical reaction and residue of etched surface was investigated with x-ray photoelectron spectroscopy (XPS) and secondary ion mass spectrometry (SIMS). As mole fraction of BCl@sub 3@ varied, boron effects with respect to residue were investigated by etched profile of SEM (scanning electron microscopy) image. In order to analyze the effect of radical density of Cl and ion current density in plasma of various gas chemistries, optical emission spectroscopy (OES) and single Langmuir probe were utilized. Change of stoichiometry on the etched surface is discussed by comparing with OES analysis.

PS-TuP5 The Study of Optical Emission Spectroscopy in SrBi@sub 2@Ta@sub 2@O@sub 9@ Etching Using Inductively Coupled Plasma*, S.U. Shin*, *D.P. Kim, E.-G. Chang, C.-I. Kim,* Chungang University, Korea

Recent developments in real-time optical emission spectroscopy (OES) for plasma diagnostics are critically mentioned. The OES results also suggest certain chemical reactions to take place in the plasma, which can be correlated to the chemical composition of the films. In this report, since the research of SrBi@sub 2@Ta@sub 2@O@sub 9@ (SBT) thin film etching was few(specially Cl@sub 2@-base), we had studied the surface reaction of SBT thin films using the OES in high density plasma etching. Measurements were made as a function of input power, pressure, bias power, and as a function of gas ratio for Cl@sub 2@ and Ar. It had been found that this SBT etch rate appeared to be more affected by the physical sputtering between Ar ions and surface of the SBT compared to the chemical reaction in our previous papers. The change of Cl radical density measured by the OES as a function of gas combination showed the change of the SBT etch rates, therefore, chemical reactions between Cl radical in plasma and components of the SBT enhanced to increase the SBT etch rates. According to the OES spectra, Ar ion bombardment strongly effects to remove Sr, Bi, and Ta atoms, however, some of the Bi and Ta atoms react with Cl radicals and form a little of BiCl@sub x@ and TaCl@sub x@, respectively. The surface residues remaining after the etch were investigated using XPS and SIMS for all of the etch conditions used in the experimental since the SBT etching process is dominant physical Ar ion bombardments and forms nonvolatile compound. These datum can be used to confirm our previous results of the OES. The plasma density and electron temperature of inductively coupled plasmas were determined by Langmuir probes. The OES results provided a strong support to the etching mechanism in inductively coupled plasma can be used to monitor the chemical and energetic properties of the plasma, providing a basis for control of industrial process.

PS-TuP6 CF, CF@sub 2@ and SiF Densities in Inductively Driven Discharges Containing C@sub 2@F@sub 6@, C@sub 4@F@sub 8@ and CHF@sub 3@*, G.A. Hebner,* Sandia National Laboratories, usa

Laser induced fluorescence was used to measure the spatially resolved CF, CF@sub 2@ and SiF radical density in inductively driven discharges containing fluorocarbon gases. Measurements of the spatially resolved CF density were performed in C@sub 2@F@sub 6@ and CHF@sub 3@ containing discharges as functions of inductive power, pressure and bias condition on a silicon substrate. In addition, CF rotational temperatures were calculated, assuming saturated spectra. Measurements of the spatially resolved CF@sub 2@ and SiF density were performed in C@sub 2@F@sub 6@, C@sub 4@F@sub 8@ and CHF@sub 3@ containing discharges as functions of inductive power, pressure and bias condition. SiF rotational temperatures were also estimated. As the inductive coil power was increased, the SiF density in the center (r = 0 cm) increased while the CF@sub 2@ density decreased and the CF density slightly decreased. In all cases, the radical density in the center of the glow increased with pressure changes from 5 to 30 mTorr while changes in the bias power had little influence on any of the measured radical densities. The spatial distribution of the CF and SiF density peaked in the center of the discharge. The CF@sub 2@ density had a local maximum in the center of the plasma with a decreasing density at the edge of the glow. However, the CF@sub 2@ density outside the glow region was a factor of 2 - 6 higher than the density inside the glow region, depending on the gas. CF and SiF rotational temperatures were between 450 and 750 K. This work was performed at Sandia National Laboratories and supported by SEMATECH and the United States Department of Energy (DE-AC04-94AL85000). Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the U. S. Department of Energy.

PS-TuP7 Ion Compositions and Energies in Inductively Coupled Discharges Containing SF@sub 6@*, A.N. Goyette, Y. Wang, J.K. Olthoff,* National Institute of Standards and Technology

High density plasmas generated in mixtures of SF@sub 6@ with rare or simple diatomic gases are involved in many dry etching processes. Plasma etching relies heavily upon surface bombardment by positive ions from the discharge, and experimental determination of the identities and energies of ions striking surfaces exposed to these plasmas contributes to understanding and accurate modeling of these plasmas. We have measured absolute total ion current densities, relative ion intensities, and ion energy distributions (IEDs) at the grounded electrode of an inductively-coupled Gaseous Electronics Conference (GEC) rf reference cell for discharges generated in pure SF@sub 6@, and in Ar/SF@sub 6@ and O@sub 2@/SF@sub 6@ gas mixtures. Several ions of significant intensity were detected from these plasmas, and the effects of chamber pressure, coil power, and mixture ratio on the fluxes and energies of ions extracted from these discharges were investigated. For pure SF@sub 6@ discharges, SF@sub x@@sup +@ (x = 0-5) ions exhibited the highest fluxes, with S@sup +@ being the dominant ion detected. Mean ion energies were between 15 eV and 20 eV, and were most sensitive to changes in gas mixture ratio. Results of measurements from the mixtures will also be presented.

PS-TuP8 Determination and Quantification of the Etch Products of Si with a Chlorine Plasma*, G.A. Gaddy, A. Orland,* Auburn University*; R. Blumenthal,* Auburn University, usa

The chlorine plasma etching of silicon has been studied utilizing a novel technique. This technique, supersonic pulse plasma mass spectrometry, allows for the in-situ sampling of the etch plasma at varying heights above the silicon substrate. It has been demonstrated previously that theoretical predictions of the percent dissociation of molecular chlorine in high-density plasmas are only observed using this mass spectral technique. The investigation focuses on the identity and concentrations of the SiCl@sub x@ (x = 1 to 4) products under typical ECR-microwave plasma conditions. Previous studies have shown SiCl to be the primary etch product. The determination of the actual percent yields of all Si etch products may be useful in determining the chemical mechanism for the release of volatile products during the etching of Si.

PS-TuP9 Ion Angular Distribution at RF Biased Electrode in Inductively Coupled Plasma*, N. Mizutani, K. Yamamuro, T. Hayashi,* ULVAC JAPAN, Ltd., Japan

Ions play an important role in the plasma etching process. The ions, which were accelerated in the sheath, bombard the substrate with high energies. The etching characteristics, that is to say, the etching rate, the selectivity, the uniformity, and so on, depend on the ion energy. The ion incident angle at the substrate will affect the characteristics in the etching of the fine pattern such as contact holes, because the ion flux at the bottom of the pattern depends on the incident angle. The ion angular distribution (IAD) had been measured at the earthed electrode in the plasma chamber by several groups.@footnote 1@ However, the IAD has never been measured at the RF biased electrode, at which the etching is done. Therefore, we measured the IAD at the RF biased electrode in the inductively coupled plasma. For the measurement at the RF electrode, the analyzer must be RF floating, that is to say, the electric potential reference of the analyzer must be the potential of the RF electrode.@footnote 2@ Therefore, we have developed such an analyzer. For 2 MHz biased Ar-O@sub 2@ plasma, the IADs were measured by using annular ion collectors that were similar to ones used in Ref. 1. The ion energy distribution (IED) at each ion collector was also measured. For the low gas pressure, 0.4 Pa, the IED was a bimodal distribution at a small incident angle (< 1°), where the vertical incidence corresponds to 0°. The bimodal distribution is due to ions that did not collide in the sheath. The ion flux at the large angle (20°) was very low compared with one at the small angle. For the high pressure, 2.7 Pa, the IED was not the simple bimodal distribution at the small incident angle, and low-energy ions increased relatively. The ion flux at the large angle increased compared with the low-pressure case. The measured behaviors of the IED and IAD can be explained by charge exchange and elastic collisions in the sheath.@footnote 3@ Comparison between the measured IAD and IED and calculated ones will be shown. @FootnoteText@ @footnote 1@ J. R. Woodworth, M. E. Riley, D. C. Meister, B. P. Aragon, M. S. Le and H. H. Sawin, J. Appl. Phys. 80, 1304 (1996). @footnote 2@ N. Mizutani, Y. Nagata, A. Kubo and T. Hayashi, Rev. Sci. Instrum. 69, 1918 (1998). @footnote 3@ N. Mizutani and T. Hayashi, Jpn. J. Appl. Phys. 38, 4206 (1999).

PS-TuP10 The Effects of Substrate Temperature on Self-Aligned Contact Etching Process*, C.W. Chu, J. Kim, K.-K. Chi, T.-H. Ahn, J.-T. Moon,* Samsung Electronics, Korea

In this paper we tried to elucidate the behavior of the selectivity of SiO@sub 2@ to underlying Si@sub 3@N@sub 4@ with the wafer surface temperature. The two kinds of specimen, non-patterned and patterned wafer, were etched in Surface Wave Plasma (Sumitomo) reacto which has an electrostatic chuck. The cooling temperature was varied from -20 to +50 in the C@sub 4@F@sub 8@ plasma. As the wafer temperature goes up, the etch-rates of SiO@sub 2@, Si@sub 3@N@sub 4@ and poly-Si of non-patterned wafer increased and the selectivity decreased, and vice versa for the patterned specimen. By increasing temperature, the decrease of etch-rate of SiO@sub 2@, the increase of selectivity of SiO@sub 2@ to Si@sub 3@N@sub 4@, and the increase of profile angle were observed in the case of the patterned specimen. These observations indicate the important role of the photo-resist erosion and sticking coefficient with a wafer temperature. The effect of carbon enrichment induced by photo-resist erosion was identified by comparing photo-resist-patterned samples with hardmask (poly-Si) patterned ones. The other fact was also supported by the polymer deposition with a low bias power etching in that, the thickness of polymer on the side-wall decreases and the thickness of polymer on the bottom increases as the wafer temperature goes up. In summary, there are two main causes in the effects of substrate temperature, and we can find out the difference between the non-patterned sample etching and the patterned sample etching from the viewpoint of surface reaction.

PS-TuP11 Molecular Dynamics Simulation of Oxide Etching by Energetic Halogens*, H. Ohta, S. Hamaguchi,* Kyoto University, Japan

We have performed molecular dynamics (MD) simulations of silicon dioxide (SiO@sub 2@) etching by energetic halogen (chlorine or fluorine) atoms (or ions) in the energy range of 50-150 eV. To classically simulate such systems, we have constructed Tersoff and Stillinger-Weber type inter-atomic potentials for systems containing Si, O, and Cl (or F) by nonlinearly fitting the inter-atomic potential functions to potential energy data obtained from ab-initio quantum mechanical calculations. Although it is experimentally known that etching rates of oxide by halogen ions are relatively low and it is generally considered that the etching mechanism is essentially physical sputtering, the goal of this study is to clarify details of oxide etching by halogen ions. Our preliminary simulation results based on the newly constructed inter-atomic potentials seem to indicate that, in addition to ordinary physical sputtering, chemical etching is also taking place in oxide etching by halogens. As oxygen atoms with two atomic bonds are more likely to be removed by physical sputtering than silicon atoms with four atomic bonds, oxygen atoms are first removed from the oxide surface by physical sputtering. The remaining excessive silicon atoms are then removed efficiently by the combination of physical and chemical sputtering by halogen ions, as in the case of silicon etching by energetic halogen ions, generating SiCl@sub x@ (SiF@sub x@) compounds as etching products. We have also observed that there are considerable differences in etching mechanisms between chlorine and fluorine ions due to their difference in atomic size. In the meeting, we shall present numerically obtained macroscopic etching properties such as etching rates as well as details of the microscopic etching mechanism and compare the simulation data with experimental observations.

PS-TuP12 PIC/MCC Simulation of a 2D Axially Symmetric Dually Frequency RF Plasma Processing System*, **S. Sunohara**, S. Hamaguchi,* Kyoto University, Japan

We have developed a Particles-In-Cell / Monte Carlo Collision (PIC/MCC) simulation code for a two-dimensional (2D) axially symmetric radio frequency (RF) driven plasma processing tool. Especially of interest for application of the simulation code is the narrow gap dual frequency reactive ion etching (RIE) system, which is known to achieve well-controlled highly selective SiO@sub 2@ etching with fluorocarbon radicals diluted in Ar discharges. In typical processing conditions for SiO@sub 2@ etching, a gas mixture(mostly Ar, a few % fluorocarbon and oxygen) is introduced to a chamber with the electrode gap of about 2 cm (for 200 mm wafer processing) and the plasma is essentially generated by the primary electrode, which is connected to a higher-frequency, higher-power RF source. The wafer is placed on the secondary cathode and ion bombardment on the wafer is controlled by the RF power applied to the secondary cathode. The narrow gap RIE system has a large surface-area-to-plasma-volume(A/V) ratio and the high performance of this system is considered mostly due to the controllability of radical generation at the wall (especially at the primary electrode) by ion bombardment. In our PIC/MCC simulation, we consider only Ar discharges since the discharge conditions are mostly determined by Ar plasmas. Electron impact ionization, excitation, elastic collision of electrons and ions with neutral species, and charge-exchange collisions are all included through the Monte Carlo collision scheme. In low-pressure discharges, we have observed in our simulation bi-Maxwellian electron energy distributions, which implies the collisionless energy transfer to the plasma is dominant. We shall present the dependence of the power deposition, ion bombardmentenergy and plasma uniformity on the gap width, RF frequencies, and RF power.

PS-TuP13 Effect of Time-varying Axial Magnetic Field on Photoresist Ashing in an Inductively Coupled Plasma*, **S.-G. Park**, H.-Y. Song, B.-H. O,* Inha University, South Korea

Time-varying axial magnetic field coupled with ICP has been found to provide more uniform and higher density plasma with lower electron temperature.@footnote 1@ Weak axial magnetic field can be obtained by a pair of current flowing Helmholtz coils attached to the chamber. This scheme has been applied to etch SiO@sub 2@ and silylated photoresist, where processing pressures are below 50 mTorr and ions are major reaction species. In this work, this method is applied to photoresist ashing, where processing pressure is usually higher than 1 Torr and down stream oxygen radicals are important species. It is found that axial magnetic field improves the ashing rate by 25% and uniformity of 4% over 8" wafer, and that the optimun frequency of the magnetic field is 60Hz. Optical emission spectroscopy is used to characterize the effect of the magnetic field. Effect of aluminum baffle inserted between plasma and wafers is also investigated in this system. @FootnoteText@ @footnote 1@ Beom-hoan O, Jae-seong Jeong, Se-Geun Park, "Improvement of ICP plasma with periodic control of axial magnetic field", Surface and Coatings Technology, 120-121(1999) 752-756.

PS-TuP14 The Characteristics of Atmospheric Pressure Glow Discharge formed by Capillary Electrode*, **Y.H. Lee**, C.H. Jeong, G.Y. Yeom,* Sungkyunkwan University, Korea

In industrial plasma processes, vacuum systems have been generally used for thin film deposition, dry etching, and surface treatments. To remove costly vacuum systems and to apply to various other situations, low temperature plasmas generated at atmospheric pressure such as dielectric barrier discharges, atmospheric microwave discharges, etc. are actively studied in these days. In this study, the characteristics of low temperature atmospheric plasmas generated using capillary electrodes were investigated. The characteristics of the plasmas were studied as a function of capillary aspect ratios, input power, frequency of input power, electrode distance, and gas mixtures and their flow rate, using a high voltage probe(Tektrionix P6015) and current probe(Pearsonelectronics 6600). Reactive gases such as He/ O@sub 2@ were also used and their ionization and dissociation properties were investigated using a mass spectrometer and optical emission spectroscopy (OES). The voltage between electrodes measured by high voltage probe increased with the increase of input power, the increase of electrode distance, the decrease of He flow rate, and the increase of O@sub 2@ flow rate. The increase of capillary aspect ratio also increased the discharge voltage, however, more stable capillary discharge was obtained by the increased current limiting of the high aspect ratio capillary. Increased ionization and dissociation of the plasma species could be observed by OES with the increase of input power in a He/ O@sub 2@ mixture. However, with the increase of O@sub 2@ flow rate in a constant He flow rate, the emission peaks from He decreased due to the increased electron consumption by oxygen while the emission peaks from O@sub 2@ @super -@ and O increased due to the increased ionization and dissociation rates with the increase of oxygen concentration in the He/O@sub 2@ gas mixture. Using He/O@sub 2@ gas mixtures, organic materials such as photoresist could be successfully removed.

PS-TuP15 Spatial Distribution of Carbon Species in Laser Ablation of Graphite Target*, **T. Ikegami**, S. Ishibashi, Y. Yamagata, K. Ebihara,* Kumamoto University, Japan*; R.K. Thareja,* Indian Institute of Technology Kanpur, India*; J. Narayan,* North Carolina State University

A DLC film has excellent properties like a diamond and its applications are expected in many fields. Pulsed laser deposition (PLD) is one of methods that can deposit hydrogen free DLC films. In order to optimize the process it is necessary to understand the ablation process. Many form of carbon species exist in the plume, therefore, their number densities and energy states seem to affect the characteristic of the deposited DLC films. However, it has not been well understood about relation between their behavior and the film properties. Emission spectroscopic analysis is usually used to the plasma plume measurement, but this method give no information on non-emissive. A carbon plasma plume produced by the KrF excimer laser ablation of a graphite target was measured by the laser induced fluorescence (LIF) method. C@sub 2@ molecules produced from the target were excited by a probe laser using C@sub 2@ swan band a@super 3@@PI@@sub u@-d@super 3@@PI@@sub g@. Two-d imensional LIF signals from C@sub 2@ molecules were measured using an ICCD camera at several delay time of the probe laser incidence from the KrF laser irradiation. Experimental results showed that C@sub 2@ molecules have relatively low internal and kinetic energy and locally exist near the target and its density decreased with increasing laser fluence.

PS-TuP16 Controlled Plasma Characteristics by a Novel Method of Enhanced Inductively Coupled Plasma*, S.-H. Rha, C.-W. Kim, S.-G. Park, **B.-H. O**,* Inha University, South Korea

It is important to control the electron energy distribution to have high quality plasma process. A conventional inductively coupled plasma(ICP) source with 13.56MHz power is not adequate for low damage sub-half micron patterning process due to higher electron temperature. Only the pulsed plasma technique seems to provide low electron temperature, and thus low process damage. Recently, a novel method proposed by us, named as 'Enhanced-ICP', which uses periodic weak axial magnetic field added to a normal ICP source, has shown great improvement in etch characteristics. Novel changes of plasma characteristics according to the frequency of time-varying axial magnetic field have been observed by a time-resolved analysis of Langmuir probe. It is found that the plasma density is increased while the electron temperature is lowered in E-ICP. Furthermore, the spatial plasma distribution is also homogenized by this method. Many evidences on improvement of electron energy distribution and spatial plasma distribution will be discussed for various cases using time-resolved analysis of Langmuir probe and optical emission spectroscopy. Theoretical analysis for this phenom is presented in this paper.

PS-TuP17 Radio Frequency Biasing of an Ion-Ion Plasma*, B. Ramamurthi,* University of Houston*; V. Midha,* General Electric*; D.J. Economou,* University of Houston

A one-dimensional fluid model for simulating the effects of RF bias applied to an ion-ion plasma was developed. The full ion momentum and continuity equations were coupled to the Poisson equation for the electrostatic field. Special emphasis was placed on the effect of applied bias frequency. Due to the lower temperature and greater mass of negative-ions compared to electrons, the sheath structure in ion-ion plasmas changes significantly as the bias frequency is varied. For low bias frequencies (100 kHz), the charge distribution in the sheath is monotonic (switching from positive to negative) during each half cycle. For intermediate frequencies (10 MHz), when the bias period approaches the ion transit time through the sheath, double layers form with both positive and negative charges coexisting in the sheath. For high frequencies, beyond the plasma frequency (60 MHz), plasma waves are launched from the bulk plasma and the sheath consists of multiple peaks of positive and negative charge (multiple double layers). For a relatively large range of bias frequencies (up to the plasma frequency), each electrode is bombarded alternately by high energy positive and negative ions during an RF bias cycle. For bias frequencies greater than the plasma frequency, however, the electrode is bombarded simultaneously by low energy positive and negative ions with ion energies approaching the ion temperature. It was also found that the ion energy increases with the applied bias potential. At relatively high pressures (greater than 20 mTorr), the ion energy at low frequencies (100 kHz) is limited by collisions and the peak ion energy may be increased by using a higher bias frequency (10 MHz). At lower pressures, however, the effect of collisions is mitigated while the effect of ion transit time becomes significant as the bias frequency increases. In this case, a low bias frequency is favorable for extracting high energy ions from the plasma.

PS-TuP18 Comparative Study of W, WN@sub x@ and Si RIE in SF@sub 6@/Ar using Actinometry Technique*, S.A. Moshkalyov, C. Reyes-Betanzo,* UNICAMP, Brazil*; A.C. Ramos,* UNICAMP-IFGW, Brazil*; A. Diniz,* ***J.W. Swart,*** UNICAMP, Brazil

The use of tungsten thin films in micro-fabrication attracts much attention. For etching of W and WN@sub x@ films, SF@sub 6@ is commonly used which provides high etch rates. However, for RIE reactors considerable undercutting of W/WN@sub x@ in SF@sub 6@ was usually reported. The objective of this study was to find conditions of anisotropic etching of tungsten films using conventional RIE medium-pressure reactor. To characterize the density of fluorine radicals in the plasma, an optical emission spectroscopy (actinometry) was employed. To provide considerable variation of radical/ion fluxes to the processed surfaces, the SF@sub 6@/Ar ratio was varied widely. Two sets of experiments were performed keeping either RF power or DC bias constant while changing the SF@sub 6@/Ar ratio. The results show that the silicon etch rate is nearly proportional to the fluorine radical density with only the minor effect of the DC bias (ion energy). Thus in the Si-F system the chemical (spontaneous) etching is the dominant mechanism. In contrast, in tungsten etching, the role of ion-induced effects is much more pronounced. Furthermore, the tungsten etch rate dependence on a fluorine density has a threshold behavior with the threshold depending on the ion energy. This indicates that at a relatively small (not saturated) surface coverage by fluorine, the ion bombardment provides strong enhancement of surface processes leading to efficient formation and desorption of volatile WF@sub 6@ etch products (most likely, an ion-induced associative desorption). Under these conditions, highly anisotropic etching of tungsten and tungsten nitride have been achieved using a conventional RIE reactor at relatively high etch rates (>100 nm/min).

PS-TuP19 Improved Etch Characteristics of SiO@sub2@ by the Enhanced Inductively Coupled Plasma*, S.-B. Cho,* *H.-Y. Song, S.-G. Park, B.-H. O,* Inha University, South Korea

It has been known that generation of active species and passivation layers is very important for etching contact holes of high aspect ration in sub-half micron technolgy. Some of the solutions are to use high C/F ratio chemistry and/or to apply pulsed plasma technique. In this work, we suggest better and simpler method, which was time-varying axial magnetic field applied to a normal ICP source. Enhanced ICP has a pair of external coils attached to the conventional ICP, and periodic weak axial magnetic field can be obtained by changing the magnitude and direction of the current through the coils periodically. Etch rate, uniformity and micro-loading effect can be greatly improved by changing the frequency. The etched characteristics by CF@sub4@ and C@sub4@F@sub8@ plasma in E-ICP is very interesting in that the bonding energy of C-C and C-F are different and the electron distribution can be controlled in E-ICP. The SEM pictures show effective removal of micro-loading effect and micro-trench problem, for an optimized E-ICP. More details on E-ICP operation for SiO@sub2@ etch and the mixture effects of additional gas (oxygen and hydrogen) are discussed further.

PS-TuP20 Silicon Surface Roughness Induced by Reactive Ion Etching in SF@sub 6@ and SF@sub 6@/O@sub 2@ Plasmas*, S.A. Moshkalyov,* UNICAMP-University of Campinas, Brazil*; P. Verdonck, R.D. Mansano,* University of São Paulo - USP, Brazil*; M. Cotta,* UNICAMP, Brazil

With the trend of continuous minimization of device structures in micro-fabrication, surface roughness induced by plasma processing becomes an important issue. The problem is of particular importance in the case of deep trench etching of silicon for MEMS applications. Mechanisms of roughness formation and development during plasma processing are not well understood. Surface roughness is closely related to the energies and flux densities of ions and reactive radicals coming from the plasma to the processed surface. A study of the evolution of surface morphology can provide better understanding of etching mechanisms. New opportunities for this kind of study arose with the recent introduction of high-resolution local probes like AFM, which allow to obtain real spatial surface images. Experiments were performed in a RF-driven RIE plasma etcher with SF@sub 6@ and SF@sub 6@/O@sub 2@ gas mixtures at medium gas pressures (50-150 mTorr). Small (100) silicon samples with an Al mask were etched with etch time varying from 2 to 30 min. After the process, etch rates were measured and surface morphology was analyzed by AFM in frames ranging from 2x2 mkm to 40x40 mkm. The results show a significant difference in roughness evolution for SF@sub 6@ and SF@sub 6@/O@sub 2@. For both cases, the roughness parameter rises almost linearly with time, but its rise is faster for oxygen contaning mixtures. For short etching times (2 min.) and small/medium oxygen content (10-30%) the rms roughness parameter was even slightly smaller for gas mixture (21-24 nm) than for pure SF@sub 6@ (26 nm). Furthemore, in the former case the surface morhology is distinctly more regular. The mechanisms reponsible for the formation of surface roughness in both cases are discussed.

PS-TuP21 Transmission Line Effects and Chlorine Plasma Characterization in an Inductively Coupled Plasma Etch Reactor*, M.H. Khater,* *L.J. Overzet,* University of Texas at Dallas

Transmission line (i.e. standing wave) effects in inductively coupled plasma sources impact the plasma and processing uniformity. In this work we show standing wave effects on the symmetry and uniformity of power deposition, plasma parameters, and polysilicon etch in chlorine plasma. A new ICP source design, which allows better control of field profiles azimuthal symmetry, is compared to a standard spiral planar coil on an industrial plasma etch reactor. B-dot probe measurements of the free space electromagnetic fields in (r,@theta@) plane for both sources showed improved azimuthal symmetry for the new source. The planar coil generated an azimuthal electric field, E@sub theta@, with a local maxima near the grounded (i.e. high current) lead and a significant azimuthal variations. A three-dimensional electromagnetic field model that includes standing wave effects was developed for both sources. The sources were modeled as uniform transmission lines and the current variation along their lengths was estimated from standard transmission line theory. The model showed good agreement with the measured field profiles. Langmuir probe measurements of chlorine plasma parameters spatial profiles near the dielectric window also showed improved azimuthal symmetry of power deposition with the new source. Parametric characterization of chlorine plasma parameters and their spatial profiles generated with the new source will also be shown. Plasma parameters and their spatial profiles exhibited different scaling behaviors with power and pressure in the power deposition region and the wafer plane. Polysilicon etch rate profiles on 150 mm wafers showed improved azimuthal symmetry and uniformity with the new source.

PS-TuP22 Penetration of Electromagnetic Fields in ICP, Weakly Magnetized ICP, and Low-B Helicon Discharges*, J.D. Evans,* *F.F. Chen, D. Arnush,* University of California, Los Angeles

Due to renewed interest by the plasma processing community, the physics of the penetration of electric and magnetic fields in low pressure, weakly ionized plasmas is an area of active research. Penetration of induced B-fields in ICP, weakly magnetized ICP, and low-field helicon discharges is investigated in a device consisting of a dome-shaped Pyrex top attached to a magnetic bucket. The antenna consists of a multi-turn loop of wire wrapped around the top (radius = R@sub top@), and B@sub o@ is produced by a magnet coil located near the antenna. B@sub z@-dot probes are used to measure B@sub z@-field profiles. B@sub z@ decays approximately exponentially with decreasing R in most cases. Characteristic decay lengths of B@sub z@ (L@sub sd@) are measured as P@sub o@ is varied. Good agreement between experiment and collisional skin depth theory is observed for f@sub RF@ = 2MHz when non-uniform density profiles are taken into account. Experimental values greatly exceed collisional theoretical predictions for f@sub RF@=6.78MHz, in qualitative agreement with anomalous skin effect (ASE) theory. Variations of L@sub sd@ with B@sub o@ have also been measured, and good agreement between experiment and collisional theory is observed in most cases. Regions of enhanced B@sub z@ ("wings") are observed near the edge for B@sub o@>0, in qualitative agreement with code predictions when axial boundary conditions are accounted for. As B@sub o@ increases, L@sub sd@ increases, and B@sub z@ in the interior increases. Coupling to a low-B@sub o@ helicon mode is expected when L@sub sd@ @>=@ R@sub top@. Under these conditions, the B@sub z@-field amplitude behavior changes from evanescence to propagation. At higher powers and neutral pressures, large phase shifts in B@sub z@, apparent "nodes" in B@sub z@ amplitude profiles, and other interference-type phenomena are observed, even in highly collisional regimes where ASE is not predicted to occur.

PS-TuP23 Ion-Ion Plasma Formation in Chlorine in an Inductively Coupled Plasma Etch Reactor*, M.H. Khater, S.K. Kanakasabapathy,* ***L.J. Overzet****,* University of Texas at Dallas

We will show time-resolved characteristics of pulsed chlorine plasmas in an industrial, inductively coupled plasma etch reactor. Using pulsed-plasmas may enhance processing and reduce charge-up damage of sub-micron features. Electron free or "ion-ion" plasma forms during the afterglow of highly electronegative discharges (e.g. Cl@sub 2@) due to electron attachment. The electron loss can be characterized by a "transition time" after which ion-ion plasma exists within the reactor. Such electron free plasma can provide both positive and negative ion fluxes to a substrate potentially reducing charge-up damage as well as enabling negative ion assisted processing. The transition time to ion-ion plasma (8-25 µsec) is mostly dependent on pressure and power while varying only slightly with pulse frequency and duty ratio. Larger Cl@sub 2@ concentrations at high pressure and/or lower power discharges result in smaller transition times due to dissociative attachment. Measurements of the plasma parameters time evolution were obtained at 1 cm above the substrate for 500 W peak power, 1 kHz pulse frequency and 50% duty ratio. The ion densities generally decreased as expected during the afterglow, except they increased slightly near the end of the afterglow at higher pressures. This suggests a transport of ions from the source towards the substrate. Spatio-temporal measurements showed electron and ion density profiles that peaked at the center during the active glow with similar uniformities to those obtained in CW operation. The ion density uniformity improved gradually during the beginning of the afterglow (~ factor of 2) but degraded back to active glow values near the end of the afterglow. This is likely related to the ion loss mechanisms. Ion-ion recombination should tend to flatten the ion density profile in the early afterglow whereas ion loss due to diffusion should tend to cause a peak in the center and dominate at the end of the afterglow.

PS-TuP24 Effect of Temperature (or Heat) on the Etch Rate of Iridium and Platinum in CF@sub 4@/O@sub 2@ Plasma, *H. Ying, J.S. Maa,* ***F. Zhang****, S.T. Hsu,* Sharp Laboratories of America, Inc.

Iridium and platinum films are often used as electrode materials in ferroelectric devices. In this work, we demonstrated that the substrate temperature plays an important role in the etching of iridium and platinum when etched in a CF@sub 4@/O@sub 2@ plasma. The etching was performed in an Electron Cyclotron Resonance (ECR) plasma reactor. The wafer was placed on a heated chuck during etching. Wafer temperature was maintained in the range of 70°C to 250°C before etching. An RF power was applied to the wafer chuck to generate a self-bias potential. At temperatures below 100°C, the iridium etch rate was low (~200 Å/min). The etch rate increased with the increase of temperature, and reached ~1500 Å/min at above 200°C. Platinum showed a low etch rate below 150°C, then also increased to ~1500 Å/min at higher temperature. In both cases, there is a transition from low etch rate to high etch rate. The transition occurred at a slightly higher temperature for the case of platinum etching. The increase of etch rate at higher temperature was believed due to the formation of volatile compound of IrF@sub 6@ and PtF@sub 6@.

PS-TuP25 Process Performance Evaluation of Low Damage Sources*,* ***X. Tang****, D. Manos,* College of William and Mary

We have performed a comparative study to characterize and evaluate the performance of two low damage sources, a surface reflection neutral source and a pulsed ICP source. The neutral stream was characterized using sensitive momentum and microcalorimetric energy analyzers to detemine that the neutral energy of our source is tunable between 3-6 eV and that the neutral flux is on the order of 3 x 10@super 15@cm@super -2@ s@super -1@. These results are in excellent agreement with earlier published flux values@footnote 1@ inferred from the stripping rate measurements and are also in excellent agreement with our previous Monte Carlo simulations.@footnote 2@ A pulsed rfi plasma source (200Hz to 10kHz) was also characterized using a Langmuir probes deploying two different data analysis methods to extract plasma density and electron temperature and to follow mode transitions in the source operation. The probe measurements indicate that there is an optimal pulse frequency in our source at around 1kHz. We have performed a zero-dimensional, explicit-time, kinetic model simulation of the pulsed behavior of this source which agrees very well with the observed values of the density, temperature, and trends of pressure and power dependence and with the temporal behavior as a function of pulse length and duty cycle. Experimental studies comparing the neutral stream to direct and downstream plasma exposure indicates that fast neutrals induces much lesss damage than exposure to the pulsed plasma source and that most of the damage from neutral operation comes from exposure to UV photons. Preliminary experiments using the fast neutral bombardment to do low-temperature growth of both stable and metastable films in a charge-free environment will also be presented in this paper. @FootnoteText@ @footnote 1@X.Tang, C.A.Nichols, and D.M.Manos, J. Appl. Phys. 86:2419, 1999 @footnote 2@C.Nichols and D.Manos, J. Appl.Phys. 80:2643,1996.

PS-TuP26 The Effects of Electrostatic Bias on the Radial Plasma Potential Profile in a Helicon Plasma*,* ***S.W. Lee****, S.H. Jun, S.H. Uhm, Y. Lee, H.Y. Chang,* Korea Advanced Institute of Science and Technology, Republic of Korea

The effects of electrostatic bias on the radial plasma potential profile has been studied in a helicon plasma. Two types of electrode - ring and planar type - were used. Electrodes were floated, negatively, and positively biased. The radial profile of ion density and plasma potential were measured with Langmuir probe. The ion velocity distribution function was measured with Doppler shifted laser induced fluorescence technique. The floating and negatively biased electrode gives similar result on plasma potential and ion density. The positive bias increases the plasma potential as high as the electrode voltage. The hollow plasma potential profile was formed when ring electrode was used. The profile is affected by gas pressure, ion density profile, static magnetic field, electron temperature, ion temperature, and ion flux. We could explain the phenomena with the results of LIF and Langmuir probe measurement.

PS-TuP27 New Large Area Plasma Source*,* ***Y. Lee****, D.S. Lee, S.W. Lee, H.Y. Chang,* Korea Advanced Institute of Science and Technology, Republic of Korea

A new large area plasma source for 300mm wafer processing were developed and studied. The antenna system of the source consists of 3-turn circular coils connected parallelly and the outer coil connected with series to an additional capacitor which is able to controll the antenna current distribution. It was found that the source have several advantages compared to other popular plasma sources. Firstly, the current distribution of the antenna by changing capacitance of the capacitor can be controlled so that the good spatial uniforminty of electron density is obtained. Secondly, the source has very low antenna voltage because the antenna has very low impedance near LC resonance point. At 3 - 30 MHz and 2 - 20 mTorr of argon, electron density uniformity within 3% was achieved.

PS-TuP28 Antenna Configurations for Large Area rf Inductive Plasma Sources*,* ***M.M. Patterson****,* University of Wisconsin, Madison, US*; T. Lho, A.E. Wendt, N. Hershkowitz,* University of Wisconsin, Madison

Industrial demands for uniform, high density, low pressure plasma processing over large areas (roughly 300 cm diameter circular substrates) motivate the study of alternatives to the standard spiral antenna design for inductive plasmas. Scaling of the spiral design suffers from several complications including increased voltage requirements (and therefore increased capacitive coupling). In addition, standing wave current variations along the length of the antenna exacerbate azimuthal nonuniformities along the increased spiral length. A possible solution to these problems is to change the connection between the concentric circular antenna loops from serial (spiral) to parallel. This lowers the net inductance (decreasing voltage requirements) and allows for control over the current in concentric loops by connecting an appropriate lumped inductor between them, enhancing uniformity. We have constructed several circular loops, 10, 20, 30, and 40 cm in diameter for use in a planar inductive plasma source of 64 cm inner diameter. Several types of connections are possible: two loops can be connected either in series or parallel, loops can be driven singularly, and more than two loops can be connected and driven in some combination of serial and parallel connections. Langmuir probe measurements of radial ion saturation current profiles in argon discharges show that good uniformity can be achieved over 30 cm diameter circular areas by choosing the appropriate inductor. Preliminary results also indicate that the ratio of inner and outer loop diameters significantly affects uniformity. We will present results that compare the spatial electron density profile with parallel versus serial connection, loop diameter, and the ratio of inner and outer loop diameters, for both serial and parallel connections.

PS-TuP29 Dry Etching of SrBi2Ta2O9 Thin Films in Cl2/NF3/O2/Ar Inductively Coupled Plasmas*,* ***Y.-H. Im****, R.-J. Choi,* Chonbuk National University, Korea*; Y.B. Hahn,* Chonbuk National University, Korea, South Korea*; J.K. Lee,* Korea Institute of Science and Technology

Inductively coupled plasma etching of SrBi2Ta2O9 (SBT) films for FRAM applications has been carried out in Cl2/NF3/O2/Ar discharges. The etch characteristics and ferroelectric properties of SBT films prepared by magnetron sputtering were investigated in terms of etch rate and P-E hysteresis curve. The etch rates were dependent on plasma parameters such as ICP source power, rf chcuk power and etch gas combinations. Ar plasma showed fastest etch rate, but resulted in severe damage to ferroelectric layers. Addition of oxygen to the etch gas combination reduced etch damage. The electrical properties of the SBT films were quite dependent on etch conditions. The decreased remanent polarization of etched Pt/SBT/Pt structure was rectified after annealing in oxygen atmosphere.

PS-TuP30 Ionized Magnetron Sputter Deposition of MgO for Protective Layers in PDP*, J. Joo,* Kunsan National University, Korea

MgO is known to be a good candidate for protective materials in Plasma Display Panel industries. Electron beam evaporation has been used to deposit MgO on glass substrates, but it has some problems in large scale production equipment for panels larger than 55 inch in diagonal. Currently, in-line type magnetron sputtering machine appears to be a solution in thickness uniformity point of view. HCD based ion plating was tried and produced very dense layer of MgO along with longer service life as a protective layer. In this study, reactive ionized PVD is tried in depositing MgO using 2 MHz ICP source along with bipolar pulsed dc sputtering power source for Mg metal target. Characteristics of deposited MgO was analysed by XRD, AFM, transparency and erosion rate. As an in- situ analysis, optical emission spectroscopy was used to monitor dissociation level of oxygen and ionization level of sputtered Mg. In mass flow rate of Ar:O2 = 10 : 2, transparent, hard MgO films were obtained lower than 300C of substrate temperature. Also the post treatment using in-situ oxygen ICP was tried to stabilized the as-deposited surface of MgO. Crystal preferred orientation varied from (111), (200) to (220) and by optimizing the plasma condition, films having similar crystalinity of bulk (JCPDS data) was successfully obtained.

PS-TuP31 Plasma Characterization and Film Structure Control for ZrO2/Y2O3 Laser Ablation in Different Environments*, A.A. Voevodin,* *J.G. Jones, J.S. Zabinski,* Air Force Research Laboratory, WPAFB

Laser ablation deposition of highly oriented yttria stabilized zirconia (YSZ) films is important for various technological applications and depends critically on the selection of background environment, with low pressure oxygen being the most common choice. Here, the spatial-temporal distribution of YSZ ablation plasma chemistry, excitation states, and energy was determined for ablations in vacuum, low pressure O2, and low pressure Ar. For this purpose, fluorescence spectroscopy, element specific imaging techniques, and time-of-flight experiments were used. It was found that an Ar background considerably promotes excitation and ionization of zirconium during the first 1-3 ï-s after the laser strike. There is much less zirconium excitation in an O2 background, where a large fraction of atomic oxygen with a broad spatial distribution was found. ZrO and YO molecules were observed in both environments. Kinetic energies of neutral species were reduced by about a factor of two in Ar and O2 backgrounds compared to vacuum. This was not observed for Zr1+ species, which maintained about 100-120 eV mean kinetic energy nearly independently of the background. The results of the plasma analyses were used for the film composition and structure control. In particular, films with [001] orientation, with respect to the substrate surface, were produced at near room temperature on various single crystal and polycrystalline substrates. Correlation between deposition parameters, plasma characteristics, and film properties are discussed.

Surface Engineering
Room Exhibit Hall C & D - Session SE-TuP
Poster Session

SE-TuP1 General Rule to Predict Under-layer Segregation on Film Surface*, M. Yoshitake,* ***Y.-R. Aparna****, K. Yoshihara,* National Research Institute for Metals, Japan

Film deposition with multi-layer structure is widely utilized in many industrial fields such as electronic device and magnetic film. Diffusion and reaction of under-layer metal sometimes cause troubles and considerable efforts are made to prevent diffusion and reaction. In catalysis field, on the other hand, surface segregation of one component in alloys or bi-layer thin film is decisive factor for its catalytic ability. We studied surface segregation of under-layer metal on the top of a film in a vacuum with Auger electron spectroscopy (AES) and/or X-ray photoelectron spectroscopy (XPS). When surface segregation of under-layer metal was observed, no significant interfacial reaction between under-layer and top layer was detected. Metallic films of sub-micron or micron order thickness were deposited on polished metallic substrates. Al, Ti, Cr, Ni, Cu, Nb and Fe were used as a substrate material, and Al, Ti, Cr, Cu, Zr, Nb and Fe were used as a film material. More than 25 combinations of film-substrate materials have been investigated. From the viewpoint of phase diagram, three types of combinations are included in those combinations, i.e., two elements in solid solution, two elements in separation, and two elements in an intermetallic compound. General rule to predict under-layer segregation on film surface is discussed based on adsorption energy. This rule is quite different from that for segregation in bulk alloy.

SE-TuP3 Role of Surface Condition in Diamond Nucleation during Bias-enhanced Nucleation*,* ***N. Ali****, W. Ahmed,* Manchester Metropolitan University, UK*; Q.H. Fan,* University of Aveiro, Portugal*; C.A. Rego,* Manchester Metropolitan University, UK

Thin polycrystalline films of diamond have been deposited on copper substrates using hot-filament chemical vapour deposition (HFCVD) system. It is known that substrate surfaces require some form of pre-treatment prior to diamond CVD. Substrate biasing has been extensively used to enhance diamond nucleation density. Majority of the work published, to date, relating to diamond nucleation by means of bias-enhanced nucleation (BEN) looks at either negatively or positively biasing substrates such as silicon where the surface biased is smooth. However, there is very little work been carried out which investigates the effect of surface roughness and surface impurities on diamond nucleation during the BEN process. We negatively bias polished copper substrates, where the polishing materials used were diamond paste, diamond powder and silicon carbide. Our preliminary results have shown that by amalgamating surface polishing with biasing there is a definite enhancement in the overall nucleation density with all the commonly used polishing materials. We observed that both surface roughness and polishing material residues seeded into the copper substrates play a critical role in diamond nucleation during the BEN process. The nucleation densities were calculated from SEM images and the surface roughness values were obtained from AFM analysis. Furthermore, the quality of the diamond grains was gauged using Raman spectroscopy.

SE-TuP4 High Rate Sputtering for Ni Films by r.f.-d.c. Coupled Magnetron Sputtering System with Multipolar Magnetic Plasma Confinement*, K. Kawabata,* *T. Tanaka,* Hiroshima Institute of Technology, Japan*; A. Kitabatake, K. Yamada, Y. Mikami,* Hiroshima Sanyo Vacuum Industries Co., LTD., Japan*; H. Kajioka, K. Toiyama,* Western Hiroshima Prefecture Industrial Institute of Technology, Japan

It is difficult to prepare ferromagnetic films such as Ni with the conventional magnetron sputtering at a low pressure and at a long substrate-target distance. Ni films were prepared by an r.f.-d.c. coupled magnetron sputtering with a multipolar magnetic plasma confinement (MMPC) at the low pressure of 6.7x10@super -2@ Pa and at the long distance of 120 mm, where the permanent magnets were placed around a Ni target (200mm, 5mm thick) outside the chamber. R.f. power and d.c.

bias were applied simultaneously to the target where an r.f. power of 60W was utilized to stabilize the plasma discharge. The deposition rate of Ni films significantly increased with the increasing target d.c. bias voltage (V@sub T@) because the target current increased with the V@sub T@. The highest value of the deposition rate was about 250 nm/min at V@sub T@=-850V. The increase in the deposition rate with V@sub T@ might be attribute to enhanced gas ionization due to a strong magnetic confinement of the plasma. It was found that the high rate sputtering for Ni films is possible at the Ar gas pressure of 6.7x10@super -2@Pa. The resistivity for all the films deposited at different d.c. bias voltages was 7.1-8.2µm@ohm@cm whose values were close to the bulk value of 6.9µm@ohm@cm. The intensity of the Ni (111) plane observed from X-ray diffraction patterns markedly increased with the V@super T@ and the value of the grain size estimated from the plane was 32-75nm. Therefore, it is shown that the sputtering system with MMPC has some advantages, in comparison with conventional magnetron sputtering, such as high deposition rate, plasma discharge stability, and the preparation of high quality magnetic thin films.

SE-TuP5 The Properties of the Wettability and Corrosion Resistance of Surface Preparation and PVD Coatings on Mold Steel*, **S.-M. Chiu**, C.-H. Lin, W.-C. Lo, Y.-C. Chen,* Metal Industries Research & Development Centre, Taiwan

During the production of IC components, packaging process is used for protection IC chips from harmful environments.Molding,trimming,and forming stages are three sequential works of packaging process.There are many factors affect moldability including molding die,mold condition,EMC,package design,and operator status.The function of molding die is to capsulate IC chips with thermosetting epoxy molding compound(EMC).The EMC is composed of many additives will abrade and corrode the molding die.It is important to extend the duty life of molding die for upgrading the production rate. In this study we compare several mold steels such as high-speed steel,stainless steel,tungsten carbide,and ceramics.Electrical discharging machining(EDM) and shot peening processes prepare the different surface roughness of mold steels. Some commercial surface treatment are preformed for comparing the surface characteristics of treated mold steels. There are including electroplated hard chromium,plasma nitriding,PVD coatings,and PCVD coatings.The contribution of these factors and their interactions to the contact angle,salt spray test,and wear test are determined.In the research of wettability shows,the influence of surface roughness on contact angle is to effect an increase in the contact angle from 77° to 110° as the roughness increases from an Ra value of 0.05µm to 2.0µm.The surface treatment can obviously reduce the influence of surface roughness on the contact angle.PVD Cr-based coatings show the highest contact angle value,above 120° ,even better than PTFE polymer material.PVD Cr-based coatings and plasma nitriding can effectively improve corrosion resistance of molding steels.To optimize the surface charactristics of PVD Cr-based coatings on molding die and be used in the IC packaging production lines.It shows that about 50% of production shots,comparing with electroplated hard chromium coating,before needing to clean the molding die.

SE-TuP6 On the Shielding Influence of Charged Particles on the Kinetics of the Oxide Film Growth*, **D.G. Mukhambetov**, O.V. Chalay,* Karaganda Metallurgical Institute, Kazakhstan

The object of this work was to investigate kinetics of the two phase oxide film growth on the @alpha@-Fe surface at the temperatures of 650 - 750 K. It is experimentally attained that film thickness h - time oxida- tion @tau@ relationship in the range denoted above is logarithmic function, whereas Kabrera and Mott's theory gives square law of the film growth. In our work analytical treatment of obtained data was made on the basis of this theory, but we suppose that self-deceleration of the film growth is caused not by attenuation of the electric intensity in the film because of increase of h but by shielding influence of the space charge of diffusing ions and elec- trons in that oxide film. With that aim in view the Debye shielding distance for plasma substance state in the oxide film was taken into consideration. Logarithmic law of the oxide film growth was derived. Estimating calcula- tions of this law parameters quantitatively corresponding with the literature data were made . The obtained results were used in the development of the surface oxidation technology of the electric steel.

SE-TuP8 Characterization of Plasma-nitrided Iron by SEM, XRD and XPS*, L.C. Gontijo,* Centro Federal de Educacao Tecnologica do Espirito Santo, Brazil*; **P.A.P. Nascente**, R. Machado,* Universidade Federal de Sao Carlos, Brazil*; E.J. Miola, L.C. Casteletti,* Universidade de Sao Paulo, Brazil

Plasma nitriding technique has been used to improve the tribological and mechanical properties of materials, specially iron-based alloys. In this work, the Pulsed Glow Discharge (PGD) technique was used for nitriding pure iron. Four samples were nitrided in a gas mixture of 80 % H@sub 2@ and 20 % N@sub 2@ under a pressure of 400 Pa, discharge frequency of 9 kHz, and temperature of 853 K. Samples 1, 2 and 3 were nitrided for 30, 60 and 90 minutes, and then quenched in situ. The fourth sample was nitrided for 90 minutes and then quenched in air. The nitrided iron samples were characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). SEM micrographs showed differences in the surface morphologies for the samples which were quenched inside the chamber. However, when the results for samples 3 and 4 were compared, it was noticed an even more significant change in the surface morphology, which demonstrates the importance of the cooling rate on the formed layer. XRD identified the Fe@sub 4@N phase in all samples. Besides this phase, also the Fe@sub 3@N, Fe@sub 2@O@sub 3@ and Fe@sub 3@O@sub 4@ phases were detected in the sample quenched in air. XPS was employed to obtain chemical-state and quantitative information of the plasma-nitrided iron surfaces.

SE-TuP9 Surface Charge Assisted Ion Deposition: A New Possibility of Film Structure Control*, **I.G. Levchenko**,* Kharkov State Aerospace University, Ukraine*; M. Keidar,* University of Michigan

The method proposed namely Surface Charge Assisted Ion Deposition consists in using the surface electrical charge as a tool for thin film micro-structure and characteristics control. It was shown that the substrate electrical charge provides the powerful and convenient possibilities of nuclei distribution function control resulting in thin film growth with the required characteristics. Using the specified surface charge - film thickness function it is possible to influence the nuclei distribution function. Criterions of electrical controllability were determined on the basis of nucleus electrical balance. It was shown that the method can provide realization of the time-divergent and time-convergent distribution functions. Interesting are the modes provides the equalization of distribution function following by the uniform growth. The possibility to create composite films consisting of bearing very hard matrix such as TiN or TiC filled with the solid-state lubricant such as Cu is shown. The Surface Charge Assisted Deposition provides formation of high-uniform bearing matrix characterized by the high hardness and tensile strength. Other filling matters can be used to provide the wide range of thin film characteristics such as high thermal conductance, temperature conductivity etc. Experimental data on comparative tests of films deposited by the Surface Charge Assisted Deposition and films deposited with the usual methods are given. The friction test shows the film wear resistance increase by factor of 1.25 due to high wear resistance and low friction coefficient of the films applied with the controlled surface charge. The experiment set-up and test conditions are shown.

SE-TuP10 Formation and Dynamic of Nuclei Distribution Function in Ion Deposition. Theoretical and Numerical Investigation*, **I.G. Levchenko**,* Kharkov State Aerospace University, Ukraine*; M. Keidar,* University of Michigan

The defining role of nuclei distribution function in thin film structure formation is now proved. The present paper is intended to develop the complete model of distribution function formation covering the whole set of the most important factors influencing the film growth. In particular, the following processes were taken into account: adsorbed particles diffusion about the substrate surface; nucleus diffusion causing the distribution function change; nuclei collisions; nuclei coalescence accompanied with the transitional quasi-liquid layer formation; etc. The study was carried out on the basis of the continuity equation for nucleus distribution function and equation for adatoms concentration in the nucleus area. Dynamic of distribution function formation was studied in the various conditions of deposition namely in high and low external flow intensity, high and low diffusion mobility, etc. The numerical simulation was performed using the above model in the most complex conditions: high rate of adsorbed particles and nuclei migration, high intensity of external flow, high substrate temperature, various ionization coefficients. The program developed provides both distribution function calculation and surface ensemble visualization in the form of series of the screen shots. The nuclei ensemble consisting 1000 particles was investigated, and surface concentration fields were calculated in the area of non-continuous film being formed. Comparisons with experimental data are shown justifying the accuracy of the model proposed.

SE-TuP11 Effect of Annealing on the Microstructure and Mechanical Property of TiN/AlN Multilayer Films Prepared by the Ion-beam Assisted Deposition*, **D.G. Kim,*** Kwangju Institute of Science and Technology, Korea*; Y.-J. Baik,* Korea Institute of Science and Technology, Korea*; T.Y. Seong,* Kwangju Institute of Science and Technology, Korea

Nano-scale nitride multilayers are considerable research interests because lattice and composition modulation induces outstanding mechanical properties. Since the microstructure of nanolayered films is metastable both mechanically and thermodynamically, the thermal effect can be an important issue. In this study, we investigated the mechanical property and the thermal stability of the TiN/AlN multilayer films. TiN/AlN multilayers were prepared on (100) Si wafer by ion-beam assisted deposition (IBAD), evaporating alternatively Ti and Al metals with nitrogen and Ar ions bombardment. The multilayers were designed to have layer sequences in different bilayer periods (l) from 3.6 to 50 nm. In addition, the samples, having 3.6 and 20 nm periods, were annealed at temperatures between 800 @super o@C and 1100 @super o@C. Nano indentation hardness was employed to acquire the mechanical property of the samples. X-ray diffraction and cross-sectional transmission electron microscopy were also used to investigate the microstructural changes of the TiN/AlN multilayers with bilayer periods. The hardness for the multilayer films with ¥ë @>=@ 6 nm was around 22 GPa, whilst the hardness for the samples with ¥ë@<=@ 4 nm showed higher than 30 GPa. For the sample with ¥ë@<=@ 4 nm, a strong and narrow superlattice (111) peak was observed. However, the peaks of the hexagonal AlN and TiN were absent in this diffraction pattern. This result showed that the (111) oriented multilayer film composed of the TiN and cubic AlN was formed and these coherently bonded superlattice made the hardness with ¥ë@<=@ 4 nm sharp increase. There was no observable change in the micro-structure of the samples annealed at lower than 900 @super o@C, which preserved the discrete layered structure. But the interdiffusion of the multilayer was perceived at the higher temperature and led to deterioration of the mechanical property.

SE-TuP12 Impression of High Voltage Pulses on Substrate in Pulsed Laser Deposition*, **T. Ikegami**, T. Ohsima, M. Nakao,* Kumamoto University, Japan*; S. Aoqui,* Sojo University, Japan*; K. Ebihara,* Kumamoto University, Japan

DLC film coatings are of technological interest for enhancing wear resistance and corrosion resistance of metals. Pulsed laser deposition (PLD) can deposit hydrogen-free DLC films, those are expected superiority in hardness and adhesion to the substrate, by graphite ablation in vacuum ambient. In PLD, controllable parameters, laser fluence, pressure and kind of ambient gas and bias voltage to a substrate, are limited. In this research, negative high voltage (HV) pulses are applied to a substrate holder synchronously with the plasma plume to modify carbon plasma plume in the similar way to plasma immersion ion implantation. Here, a carbon plasma plume produced by laser ablation is used as a high-density plasma source. High energetic carbon ions and excited atoms can be expected to improve film properties and its adhesion to the substrate. Effect of HV pulses on the plasma plume was investigated by optical emission spectrometry, laser induced fluorescence meth od and their effect on DLC films was examined using FTIR, AFM and Raman analyses. By applying HV pulses emission from C@super +@ increased and modification was found in film properties.

SE-TuP13 Characterization of Chromium Nitride Coatings Deposited by A Hybrid PVD and Metal Plasma Ion Implantation Process*, D.-Y. Wang, **K.-W. Weng,*** National Chung-Hsing University, Taiwan

Chromium nitride coatings were deposited using a hybrid PVD and metal plasma ion implantation (MPII) process. MPII is a plasma-based ion implantation process, which supplies low energy (10-80 keV) metal ions with multiple charge states. At the initial coating stage, low dosage of MPII ion flux helps in effective surface activation and ion mixing. The interface adherence is significantly improved. A subsequent ion bombardment by MPII in conjunction with a conventional cathodic arc evaporation process provides apparent advantage of film densification and stress relaxation. The influence of ion energy of MPII source upon film properties will be conducted using mechanical and tribological tests.

SE-TuP14 Energy and Angular Distributions of Deposition Flux in Magnetron Sputtering Systems*, **R.I. Erickson**, J.R. Doyle,* Macalester College

The substrate energy and angular distribution of atoms sputtered in a magnetron glow discharge in argon is studied using Monte Carlo simulations and deposition profiles in cavity substrates. The simulation uses the TRIM code for the nascent sputter atom energy and angular distribution. The gas phase collisions are modelled using Thomas-Fermi-Dirac potentials for the higher energies and Lennard-Jones potentials for near thermal energies. Comparison of experimental deposition profiles on cavity substrates with the predicted angular distribution of arriving flux yields good agreement. The simulation results predict that the average energy of arriving atoms exhibit a dependence Bexp(-apd) down to thermal energies where p is the pressure, d is the target-substrate distance, B is the average energy of the nascent sputter atoms, and a is a constant independent of p and d. The constant a can be considered the inverse of a characteristic pd value for thermalization, and is parameterized by the atomic number of the target atom yielding a universal relation for arbitrary targets sputtered in argon.

SE-TuP15 The Corrosion Resistance of the Chromium Nitride on Carbon Steel by Cathodic Arc Deposition*, **S. Han,*** National Chung Hsing University, Taiwan, ROC*; J.H. Lin,* National Tsing Hua University, Taiwan, ROC*; S.C. Chung,* Industrial Technology Research Institute, Taiwan, ROC*; S.H. Tsai,* National Tsing Hua University, Taiwan, ROC*; F.H. Lu,* National Chung Hsing University, Taiwan, ROC*; H.C. Shih,* National Tsing Hua University, Taiwan, ROC, Taiwan,ROC

The electrochemical behavior of CrN coating on steel is investigated. The CrN coatings are deposited using a reactive cathodic arc plasma deposition technology in an industrial scale. The microstructure and crystalline of chromium nitride have been investigated using XRD, XTEM and SAD. The CrN coatings exhibit microcolumnar morphologies. The aqueous corrosion behavior of the coatings was studied in a saline (3% NaCl solution) environment by OCP and EIS measurements. The OCP measurements indicated that the CrN coatings are nobler than the uncoated substrate. The R @sub p@ of the CrN coatings is at least an order of magnitude larger than the uncoated alloy steel. Moreover, the R @sub p@ of the CrN coatings tends to decrease with immersion duration, showing that the corrosion changes from charge transfer to diffusion control process especially when the immersion time is long enough.

Surface Science
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SS-TuP1 Oriented Growth of Rod-like Second Phase Precipitate on the (1014) Calcite Surface*, **A.S. Lea**, D.R. Baer, T.T. Hurt, J.E. Amonette,* Pacific Northwest National Laboratory

An apparent epitaxial growth from solution of a Mn-rich phase on calcite (CaCO@sub 3@) has been observed by atomic force microscopy (AFM). Calcite, which is the most widely distributed carbonate mineral, interacts with and incorporates contaminants from the environment and serves as a major reservoir in the global carbon cycle. We have used an AFM equipped with a fluid cell to examine the influence of various solution contaminant ions (Mn, Sr, PO@sub 4@) on the rates of dissolution of pure calcite. Here, we report on the influence of a soluble Mn@super 2+@ impurity on the dissolution behavior of calcite. At Mn@super 2+@ concentrations well below saturation for bulk MnCO@sub 3@, the Mn@super 2+@ inhibited dissolution uniformly. However, at Mn@super 2+@ concentrations near the MnCO@sub 3@ saturation level, we observed the formation and oriented growth of rod-like precipitates on the surface. These rods grew along the [221] direction of the surface until they reached a step edge where they could grow no further. While these rods could grow many microns in length, their width was limited to 120 to 180 nm and their thickness was measured consistently at 25 Å, which is indicative of a critical thickness of growth. XPS analysis of the rod covered surfaces showed the presence of Mn with a +2 or +3 valence. EPR analysis of the bulk sample after rod formation shows an intense broad signal that is indicative of dipole-dipole alignment between neighboring Mn(II) ions and distinct from the sextuplet (commonly seen for isolated Mn(II) ions in bulk calcite) observed in the untreated sample. Together these analyses suggest formation of an epitaxial Mn(II) phase on the surface of calcite.

SS-TuP2 Photocatalytic Degradation of Self-Assembled Monolayers Anchored at the Vicinity of Titanium Dioxide Domains, as a Probe for Surface Diffusion*, **Y. Paz**, H. Haick,* Technion-IIT, Israel

The presented work demonstrates the ability of self-assembled monolayers to serve as a tool for gaining information on surface diffusion of oxidizing species formed photocatalitically on titanium dioxide. In order to study the photodegradation of molecules located at the vicinity of a titanium dioxide photocatalyst, well-defined structures comprised of alternating micro-stripes of TiO2 and silicon were prepared on silicon wafers. Onto these structures, a cross-linked self-assembled monolayer (SAM) of Octadecyltrichlorosilane (OTS) was chemisorbed. The kinetics of the photodegradation of the anchored SAM on the hybrid structure was then measured in-situ by FTIR under controlled humidity. It was found that the photogenerated oxidizing species, formed on the titanium dioxide well-defined micro-domains, are capable of inducing, within minutes, the mineralization of the aliphatic chains anchored to the inert silicon domains, even when these chains were located as far as 20 microns away from the titanium dioxide micro-zones. In contrast, no remote mineralization could be observed when the same experiments were performed with alkanethiols on gold, in Au/TiO2 hybrid systems. A mechanism, explaining these results and their dependency upon various parameters (diffusion length, temperature, humidity) is presented. The implications of these observations on the design and modeling of porous photocatalysts having "dark" pores are discussed as well.

SS-TuP3 Reactions of HCl and geminal-dichloroethylene on Pd(111) Studied by TDS, LITD, and STM*, D.E. Hunka,* University of California, Davis*; D.C. Herman,* University of North Carolina, Chapel Hill*; L.I. Lopez,* University of California, Berkeley*; K.D. Lormand, D. Futaba, S. Chiang, D.P. Land,* University of California, Davis

Small organic halides are common groundwater pollutants and remediation of these contaminants has become a popular field of study. Among these, chloroethylenes are the most abundant. Catalytic degradation on transition metal surfaces offers a promising method for the alleviation of this ubiquitous problem. The reactions of HCl and geminal-dichloroethylene on Pd(111) have been investigated using thermal desorption spectroscopy (TDS), laser-induced thermal desorption coupled with FT-mass spectrometry (LITD-FTMS), variable temperature scanning tunneling microscopy, as well as Auger electron spectroscopy and low energy electron diffraction. Although HCl is seen to desorb from the surface in four peaks during TDS, only three distinct surface species exist: two of which are dissociative in nature and one molecular surface species. HCl and H@sub 2@ are the exclusive desorption products from the decomposition of gem-DCE, and HCl is found to desorb in two desorption peaks at exposures over 0.33 L. These peaks occur at temperatures well above those expected for HCl on clean Pd(111) and are ascribed to a stepwise decomposition of gem-DCE. The two surface intermediates in this stepwise decomposition have been identified using FT-RAIRS. The first intermediate, which is attributed to a chlorothylidyne species, forms by 150 K and is not seen to decompose further until ~400 K. Further decomposition of this intermediate produces a chlorovinylidene species which does not decompose further until ~600 K. Variable temperature scanning tunneling microscopy has been used to observe the reactions of both HCl and gem-DCE on Pd, as well, with the results supporting the above assignments.

SS-TuP4 Lubrication Mechanisms of Tricresylphosphate, TCP, on Cr and Fe Surfaces at Elevated Temperatures: An Atomic-Scale View*, M. Abdelmaksoud,* *B. Borovsky, J. Krim,* North Carolina State University

TCP is a high-temperature vapor-phase lubricant which is known for its demonstrated anti-wear properties for macroscopic systems. Although this lubricant has been the subject of much research for over 40 years, the atomic-scale details of its lubrication mechanisms are far from being satisfactorily understood. In this study, we evaporated Fe and Cr substrates in UHV conditions onto Quartz Crystal Microbalances, (QCM), and then monitored the uptake rates of TCP on these substrates at different temperatures. Using an in-situ Auger spectrometer, the samples' surface chemistries were investigated in parallel with uptake rates at the various temperatures. Graphitic carbon was found to be the dominant surface constituent. To understand the role of oxygen in the lubrication process, some samples have been exposed to oxygen before TCP deposition. Comparing deposition rates of pure and oxide surfaces and the corresponding Auger scans allowed determination of whether or not oxygen has an effective part in the lubrication of these two metals with TCP. Our results suggest that oxygen is not a factor in controlling TCP interaction with Fe. Overall, we observed TCP to diffuse more readily into Fe than Cr, supporting recent conclusion by N. Forster.@footnote 1@ on the diffusion mechanisms underlying the lubricants effectiveness. In addition, we observed the TCP to greatly inhibit the uptake of oxygen from the gas phase. @FootnoteText@ @footnote 1@ N. H. Forster, Triboblogy Transactions, Volume 42, P. 10-20, (1999).

SS-TuP5 Density-Functional Study of NO Dissociation on the Al(111) Surface*, B. Razaznejad,* *B.I. Lundqvist,* Chalmers University of Technology, Sweden

A first-principles density-functional study utilizing the generalized-gradient approximation (GGA) for exchange-correlation effects is made for the energetics and electron structure of nitrid monoxide (NO) on the (111) surface of aluminum. The calculated adiabatic potential energy surfaces show that (i) when the molecule is kept perpendicular to the surface, with the oxygen atom down, there exist an activation barrier of 0.6 eV in the exit channel, while (ii) there exist a moleculer chemisorption state, identified as a "NO@sup 2-@" electron configuration, precursor to dissociation, when the molecule is kept parallel or perpendicular to the surface, with the nitrogen atom down. The complexity of the adiabatic potential energy surface indicates an interesting dynamics for NO dissociation on the (111) surface of aluminum.

SS-TuP6 Electrochemical Characterization and Surface Analysis of Bulk Amorphous Alloys in Aqueous Solutions at Different pH*, D.L. Cocke,* Lamar University*; D.G. Naugle,* Texas A&M University*; H. McWhinney,* Prairie View A&M University*; R. Schennach,* Lamar University

Bulk amorphous alloys are a new class of materials with a variety of characteristics that make them useful for applications in aqueous environments. While some bulk amorphous metals show increased corrosion resistance, there is still a lack of fundamental electrochemical studies of these materials. Three different compositions of BeCuNiTiZr bulk amorphous alloys have been studied at pH 5, 7 and 8 using Cyclic Voltammetry (CV), X-ray Photoelectron Spectroscopy (XPS) and electron microscopy. While XPS is used to determine the composition of the resulting oxide films, the CV curves are compared to the corresponding binary alloys, to pinpoint differences in the corrosion resistance of the amorphous multi-component alloy. The effect of the amorphizity, multi-component structure and the presence of elements with widely varying interfacial reactivities will be discussed.

SS-TuP8 Characterization of High Surface Area Platinum Black Electrodes for Electrochemical Sensing Applications*, P. Neuzil,* Institute of Microelectronics, Singapore*; B. Ilic, D. Czaplewski,* Cornell University*; T. Stanczyk,* Molex Incorporated*; J. Blough, G.J. Maclay,* University of Illinois at Chicago

The investigation of adsorbed high surface area noble metal nanoparticulates is important in medicine, nanotechnology, electrochemistry, microelectromechanical systems (MEMS) and sensors, biology, and in industry. In particular, high surface area noble metal electrodes have made a considerable impact in the field of microfabricated solid state, chemical and biological sensors. In our work, we investigate the properties of electrochemically deposited platinum black by atomic force and scanning electron microscopy. Initially the platinum electrodes were fabricated on various substrates utilizing developed silicon surface micromachining techniques. Platinum black was then electrochemically deposited on top of the microfabricated platinum electrodes. The platenized electrodes were subsequently used in an electrochemical cell for carbon monoxide detection (CO). The primary benefit of platinized electrodes is the increase in the surface area of the catalyst, which in turn causes an enhancement in the CO sensitivity by a few orders of magnitude. Deposition time and thermal conditioning were found to influence the quality and morphology of the platinum black layer. Methods of fractal analysis were employed to the acquired tapping mode atomic force micrographs in order to demonstrate the degree of roughness of the platinization. Morphological inclusions were readily observed in films deposited for duration of less than 60 seconds, at a bias of 1.5 V against a platinum counter electrode. Shorting of the microfabricated electrodes due to lateral outgrowth of high surface area platinum black was observed for various electrode geometries when current densities on the order of 100 mA cm@super -2@ were employed. We further show from out CO sensor performance that reproducibility of highly adherent platinized electrodes is achieved.

SS-TuP9 A Novel Technique for Producing Regular Nano-Channel Arrays*, S.A. Barnett,* *S. Sambasivan,* Applied Thin Films, Inc.

In this paper, we describe a simple method for producing large area nano-channel arrays with channel widths down to 1 nm. The synthetic method involves deposition of multilayers by magnetron sputtering where the width of each layer can be accurately controlled from 1-100nm. Subsequent to the deposition, one of the layers is preferentially etched to leave behind trenches of the other layer left intact. With appropriate choice of chemistry and etching technique,we have demonstrated the feasibility of this technique for a multilayer system. The residual layer and the intervening channels are quite planar for optimized film growth conditions, and thicknesses can be very accurately controlled. A number of applications can be envisioned for these channel arrays. For example, they should make good media for nano-stamping with the choice of a very hard material as one of the component layers. This should allow for imprinting of a wide range of materials. Initial results on nano-stamping will be presented.

SS-TuP10 In situ Investigation of Stage Formation of Eutectic Alloys during Annealing Amorphous and Crystalline Silicon with Metals, ***B.B. Bokhonov**, M.A. Korchagin,* Institute of Solid State Chemistry SB RAS, Russia

The in situ electron microscopic investigation of the formation of eutectic alloys in the system: amorphous film Si or crystalline thin foil (100)Si - particle Me (Me = Au, Ag, Cu, Al), showed the formation of eutectics is preceded by metal diffusion into amorphous silicon with the formation of metastable amorphous metal silicide. Supersaturation and decomposition of metastable metal silicide leads to the evolution of polycrystalline silicon. Morphological characteristics of liquid eutectic formation in system: crystalline silicon foil - metal particle are similar to well known morphological characteristics of the formation of etch pits in crystals. For the systems: crystalline silicon foil - metal particle (gold, silver and copper), oriented formation of the liquid evtectic are observed. The crystallization of liquid eutectic alloys leads to topotaxial evolution of metal silicide islands or compounds at the interface - eutectic alloy/silicon crystal.

SS-TuP11 The Study of ITO Targets Produced at Various Temperatures, ***J.H. Choi**,* Samsung Advanced Institute of Technology, Korea, R. of Korea; *H. Choi, J.S. Lee, J.Y. Won,* Samsung Advanced Institute of Technology, Korea; *J.C. Lee, C.B. Lim,* Samsung Advanced Institute of Technology, Korea, R. of Korea

ITO targets were produced by annealing of mixed powder of 90 wt% In@sub 2@O@sub 3@ and 10 wt% SnO@sub 2@ at various temperatures. The products were investigated by using TEM/EELS, XRD, XPS, and AES. The XRD results show that the phases of In@sub 2@O@sub 3@ and SnO@sub 2@ remain unchanged until 1300°C annealing. Whereas only In@sub 2@O@sub 3@ phase appears over 1400°C annealing. Further experiments with TEM/EELS demonstrate that in fact the In@sub 2@O@sub 3@ over 1400°C annealing is Sn-doped In@sub 2@O@sub 3@ which is dominant phase and there is another phase which is Sn-rich In@sub 2@O@sub 3@ . As the annealing temperature increases, the grain size increases, but the phases still remain. And many small spots exist inside Sn-doped In@sub 2@O@sub 3@ grains. It is In@sub 2@O@sub 3@ which is not Sn-doped. It is thought that the content of SnO@sub 2@ is more than proper to achieve Sn-doped ITO target completely.

SS-TuP12 Structure Analysis of Ta Films Deposited on Si(100), SiO@sub 2@, and Si@sub 3@N@sub 4@ Surface by Tapping Mode Atomic Force Microscopy, ***F. Wu**,* Medtronic, Inc.

Ta films deposited on Si(100), SiO@sub 2@, and Si@sub 3@N@sub 4@ surface during growth at different pressure and temperature were investigated using tapping mode Atomic Force Microscopy. The surface morphology of the films was found to depend on the subtrate surface, sputtering pressure and substrate temperature. Film stress and roughness of Ta/different substrate vs different deposition conditions were measured. The surface roughness of the films decreased with decreasing sputtering pressure and with increasing substrate temperature.

SS-TuP13 The Orientational Effects under Ion Grazing Incidence on the GaP(100) Surface, ***U.O. Kutliev**,* Urganch State University, Uzbekistan; *A.A. Dzhurakhalov,* Institute of Electronics, Uzbekistan; *B.C. Kalandarov,* Urganch State University, Uzbekistan

Research of laws of grazing scattering of ions begins with study of the form of trajectories of scattering particles. The forms these trajectories are rather difficult, as they are determined large by number correlated of collisions. This circumstance not allows to receive the analytical decision of the given task. By unique effective way of account of the form of trajectories grazing scattering is the modeling on the computer. In the present work the scattering processes on the GaP(100) surface under grazing ion bombardment have been investigated by computer simulation. The trajectories of incident positive ions Ne were simulated in the binary collision approximation. Energy and angular distributions of Ne+ ions scattered from the GaP (100) surface in the , directions and target orientations were calculated. The computational results show that in the energy spectrum the characteristic peaks corresponding to scattering of ions by the surface atomic chains and semichannels are observed. The situation and intensity of these peaks depend on the forms of the surface semichannels. This technique can be useful for investigations of semiconductor structures.

SS-TuP14 Tribocharging in Electrostatic Beneficiation of Coal: Effects of Surface Composition on Work Function as Measured by XPS and UPS in Air, ***S. Trigwell**, M.K. Mazumder,* University of Arkansas at Little Rock; *R. Pellissier,* RKI Instruments

The cleaning of coal by electrostatic beneficiation is based on tribocharging characteristics of pulverized (smaller than 120 µmm) coal particles. The variation in the charge distribution of electrostatically separated coal particles, as measured by an E-SPART analyzer, indicates that coal exhibits bi-polar charging. This appears to be in conflict with expectations in that the organic coal particles should charge positively, and the mineral particles, present as impurities such as pyrite, charge negatively, as predicted by the relative work functions of the particles (coal and mineral) and the metal surface (copper or stainless steel) used for tribocharging. UPS measurements in air on specimens of three different coal species showed the work function to be higher than predicted, approximately 5.4 eV. Determination of the coal surface composition by XPS showed the coal and the pyrite to be oxidized to different degrees. Studies by UPS and XPS, on copper, stainless steel, aluminium, and other commonly used tribocharging materials such as glass and PTFE, as well as pure pyrite, showed that the work function varied considerably as a function of surface oxidation. Therefore the reason for the bi-polar charging of the coal particles may be due a too small work function difference. The choice of a material for impaction triboelectric charging for coal or mineral separation should therefore depend upon the oxidized work function difference. The correlation between the charge distribution and work function is discussed.

SS-TuP15 The Secondary Electron Emission Characteristics for Sol-Gel Based SiO@sub2@ Thin Films, ***T. Jeong**, J. Lee, S. Yu, S. Jin, J. Heo, W. Yi,* Samsung Advanced Institute of Technology, Korea; *D. Jeon,* Myongji University, Korea; *J.M. Kim,* Samsung Advanced Institute of Technology, Korea

We have fabricated SiO@sub2@ thin films by sol-gel method with six different tetraethyl orthosilicate (TEOS) molarities, which were 0.116 M, 0.058 M, 0.029 M, 0.015 M, and 0.007 M. Each solution of the different TEOS molarity was coated on the Si substrate by a spin coater. The SiO@sub2@ layer was formed on the substrate by thermal heating at 450°C for three hours. From Nanospec/AFT Model 200 the thickness of the SiO@sub2@ film decreased as the concentration of TEOS decreased; the thicknesses of SiO@sub2@ were estimated to be 69 nm, 36 nm, 16 nm, 11 nm, 9 nm, and 7 nm for 0.232, 0.116, 0.058, 0.029, 0.015, and 0.007 molarity of TEOS solution, respectively. Finally, we measured secondary electron emission (SEE) yields for these SiO@sub2@ thin layers by bombarding electrons in the vacuum chamber which was maintained at around 110-7 torr. It was observed that the 9 nm thick SiO@sub2@ film exhibits the highest SEE yield (about 4) among six samples. This observation agrees well with our previous results obtained from thermal SiO@sub2@ films. The higher SEE yields for sol-gel based SiO@sub2@ films than thermal SiO@sub2@ films suggest that the sol-gel method is useful for secondary electron emission layer formation. In conclusion, the solution based SiO@sub2@ layer coating method is promising, especially for secondary electron emission layer for the electron multiplying devices, due to high secondary electron emission yield and its easy application to a porous surface such as alumina.

SS-TuP16 Absolute Determination of the Stoichiometry of Ultrathin Oxide Films as a Function of Thickness: Antimony Oxide on Gold, *K. Stefanov, **A.J. Slavin**,* Trent University, Canada

As the thickness of oxides in microelectronic devices decreases, it has become essential to know how oxide stoichiometry evolves with film thickness. This work uses a high-stability quartz crystal microbalance@footnote 1@ which can provide an absolute determination of stoichiometry as it evolves one molecular layer at a time. In the case of antimony films on a gold substrate, the first two monolayers of Sb oxidize as SbAuO, whereas subsequent layers oxidize as Sb@sub2@O@sub3@. @FootnoteText@ @footnote 1@ S.S. Narine and A.J. Slavin, J. Vac. Sci. Technol. A16, 1857 (1998).

SS-TuP17 Dodecanethiol on Cu(110) Studied by Low-temperature STM, ***A. Kühnle**, T.R. Linderoth, E. Laegsgaard, I. Stensgaard, F. Besenbacher,* University of Aarhus, Denmark

Monolayers of alkane thiols, primarily on Au(111), have been studied extensively as model systems for self-assembly. A number of UHV-STM investigations have been carried out at room temperature adressing the structure of different phases formed from low coverage where the molecules are lying down to higher coverage where they are standing-up.@footnote 1@ Very little is known, however, about the diffusion dynamics of the individual molecules or the quantitative details of the initial nucleation and growth of molecular aggregates on the surface. We have recently initiated a programme to investigate such questions using a home-built UHV-STM operating at variable temperatures down to 25 K. For dodecanethiol [CH@sub 3@(CH@sub 2@)@sub 11@-SH] deposited onto Cu(110) at a sample temperature of 110 K we find the formation of an ordered overlayer structure with molecules lying with their backbone parallel to the surface. There is thus considerable molecular mobility on the surface already at this temperature. We are currently extending these experiments to lower temperatures where the diffusion of individual molecules can be followed by time-lapse STM. @FootnoteText@ @footnote 1@ G.E. Poirier and E.D. Pylant, SCIENCE vol. 272, 1145, (1996).

SS-TuP18 Temperature-induced Morphology Changes for 1D Pt Islands on Pt(110)-(1x2)*, **T.R. Linderoth**, S. Horch, L. Petersen, E. Laegsgaard, I. Stensgaard, F. Besenbacher,* University of Aarhus, Denmark

The Pt/Pt(110)-(1x2) system has proven a fascinating one-dimensional model system for the study of adatom dynamics by time-resolved STM. At temperatures between 290-380 K, isolated ad-atoms and islands are restricted to the missing-row troughs where atoms show a quasi-1D diffusion behaviour@footnote 1@ while islands migrate along the troughs by a so-called "leap-frog" mechanism.@footnote 2@ Here we wish to present the results of quench-and-look experiments initiated to investigate ripening in this seemingly 1D system. When a surface with 1D Pt islands situated in the missing-row troughs is annealed at 369-395 K, we find: (a) an increase in the mean island size (coarsening) and (b) a surprising island restructuring, where adatoms move from the troughs up on top of the islands. Quantitative analysis of these findings and comparison to the known rates for island diffusion and other relevant kinetic processes interestingly reveal that the Pt/Pt(110)-(1x2) system can NOT be treated as purely 1D at the higher adatom coverages of 27±4 % used in the present experiments. Dynamic STM data, acquired at these higher adatom coverages, provides direct evidence for novel atomic-scale mechanisms leading to inter-trough mass transport. @FootnoteText@ @footnote 1@ Phys. Rev. Lett. 78, 4978 (97). @footnote 2@ Phys. Rev. Lett. 82, 1494 (99).

SS-TuP19 Friction on Diamond-Like Thin Films : Analysis by XPS*, **J.M. Campbell**, L.-S. Johansson,* Helsinki University of Technology, Finland*; J. Koskinen,* VTT Manufacturing Technology, Finland

Under humid conditions, an anomalous drop occurred in the coefficient of friction for a stainless steel ball bearing impinging on a Diamond-Like Coated (DLC) metal ring. XPS analysis of the wear area revealed minute but significant changes from the native film surface. Metal particles were present on the wear track; however, no chemical change in the DLC film was apparent. Assessment of the inelastic background shows that the metal resides on top of the DLC film. It is believed that the metal particles adsorb water from the humid atmosphere to form a lubricating layer.

SS-TuP20 Scanning Tunneling Microscopy of Single-Crystal Si@sub 3@N@sub 4@ Layer Grown on Si(111) by Nitridation*, **C.-L. Wu**, H. Ahn, Y.-C. Chou, S. Gwo,* National Tsing-Hua University, Taiwan

It has been known that ordered thin Si@sub 3@N@sub 4@ layer can be formed on Si(111) by exposing the Si surface to various nitrogen-containing gases (NH@sub 3@, NO, N, etc.) at high substrate temperatures. A variety of surface orderings ("8x8", "8/3x8/3", "4x4", and quadruplet) have been reported by previous studies using different surface-sensitive techniques, such as low-energy electron diffraction (LEED) and scanning tunneling microscopy (STM), etc. However, until now there is no proposed structure model can satisfactorily incorporate all the observed features. In this work, by using high-resolution STM images at dual bias polarities in combination with Kikuchi electron holography (KEH), transmission electron microscopy (TEM), and ab initio total-energy calculations, we have determined an atomic model for this surface, which is capable of explaining the previously observed surface orderings.

SS-TuP21 Electron- and Photon-stimulated Desorption of Alkali Atoms from Silicon Dioxide and Ice Surfaces*, **B.V. Yakshinskiy**, T.E. Madey,* Rutgers University

To investigate mechanisms for the origin of K and Na in the tenuous atmospheres of the Moon, Mercury and Europa, we are studying the electron- and photon-stimulated desorption (ESD and PSD) of alkali atoms from model surfaces: amorphous SiO@sub 2@ and water ice films (both crystalline and amorphous) grown on a metal substrate. The measurement scheme for ESD and PSD of alkali atoms includes a highly sensitive detector based on surface ionization, and a time-of-flight technique. For PSD measurements, a mercury arc light source (filtered and chopped) is used. In the present work, we focus on ESD and PSD of K atoms, and compare with our previous studies of Na desorption from SiO@sub 2@.@footnote 1@ We find that bombardment of the alkali covered surfaces by ultraviolet photons or by low energy electrons (E>4 eV) causes desorption of "hot" K and Na atoms. The velocity distributions (VD) of K and Na desorbing from the silica surface are peaked at 650 and 1000 m/s, respectively, whereas the corresponding VD for desorption from the ice surfaces have maxima at 500 and 800 m/s. These values are consistent with the "hot" components of the lunar, Mercurian and Europian atmospheres. The mechanism of desorption is identified as an electronically excited charge-transfer from the silica or the ice substrate to neutralize alkali ion, followed by desorption of the alkali atom. We conclude that PSD by UV solar irradiation is a dominant source process for K and Na in tenuous planetary atmospheres. @FootnoteText@ @footnote 1@ BVY and TEM, Nature, Vol. 400, 642 (1999).

SS-TuP22 Using Surface-modified Embedded-atom-potentials to Simulate the Adsorption and Diffusion of Gold and Lead Atoms on the Au(111) Surface*, **M.C. Robinson**,* Trent University, Canada*; K. De'Bell,* University of New Brunswick, Canada*; A.J. Slavin,* Trent University, Canada

The usual embedded-atom method (EAM) typically underestimates surface energies and surface diffusion barriers on (111) surfaces. However, the EAM potentials can be modified@footnote 1@ to provide a fit to the surface energy without modifying the zero-temperature bulk properties. These modified potentials provide much more reasonable values for other surface properties. For example, they predict a surface-layer compression in agreement with that observed in the Au(111) "herringbone" reconstruction. Molecular-dynamics simulations indicate that the preferred mode of surface diffusion is incorporation of an adatom into the surface at one location with the ejection of another atom to the surface elsewhere. In the case of Pb deposited on the reconstructed Au(111) surface, they also predict an instability in the surface energy for a coverage of about 0.05 monolayers. Comparisons are made with scanning tunneling microscopy data for Pb on the Au(111) surface. Research supported by NSERC Canada. @FootnoteText@ @footnote 1@ M.I. Haftel and M.I. Rosen, Phys. Rev. B15, 4426 (1995).

SS-TuP23 The Adsorption and Trimerization of Acetylene to Benzene on Cu(110) Monitored by X-ray Spectroscopies*, **H. Öström**, K. Weiss, L. Triguero, A. Nilsson,* Uppsala University, Sweden

We have studied the adsorption of acetylene on Cu(110) and its trimerization reaction to benzene by high resolution X-ray photoelectron spectroscopy (XPS), near edge X-ray absorption fine structure (NEXAFS) spectroscopy and temperature programmed desorption (TPD). At liquid nitrogen temperature the XP spectra show two different C 1s peaks which correspond to two nonequivalent adsorbed acetylene species. By heating the sample one species transforms into the other. This species disappears above room temperature due to the trimerization of acetylene to benzene. The reaction has been followed by time resolved XP spectroscopy. We have been able to monitor the reaction in real time, finding that benzene leaves the surface as soon as it is formed. The adsorption geometry of the different adsorbate species has been determined by polarization dependent NEXAFS spectra and the experimental results are completed by ab-initio cluster model calculations performed in the framework of density functional theory (DFT).

SS-TuP24 Study of High and Low Work Function Surfaces for HyperThermal Surface Ionization using an Absolute Kelvin Probe*, **I.D. Baikie**, U. Petermann, B. Lägel, K. Dirscherl,* Robert Gordon University, UK

We have performed a study of high (> 6eV) and low (

SS-TuP25 A Double Quartz Crystal Microbalance Sensor for Monitoring High Pressure Heterogeneous Catalytic Reactions on Real Catalysts*, **I. Zori@aa c@**,* Chalmers University of Technology and Göteborgs University, Sweden*; P. Borchardt, C. Keller, B. Kasemo,* Chalmers University of Technology, Sweden

The quartz crystal microbalance (QCM) is a piezoelectric oscillator with a high sensitivity for micro weighing (<0.01ML of H@sub 2@) and a fast response. In this work we report a novel sensor consisting of two QCMs mounted on a single, 5 MHz, AT cut quartz crystal. The catalyst consists of metallic, highly dispersed, nanosized Pt particles on an Al@sub 2@O@sub 3@ washcoat deposited on one QCM by standard wet deposition methods.

The other QCM, coated with washcoat only, was used as a reference allowing for subtraction of the frequency shift due to temperature changes, or in a constant temperature experiment, the separation of gases adsorbed on the noble metal of the catalyst from those adsorbed on the alumina support. The catalytic reaction chosen for testing of the sensor system was the high pressure H@sub 2@+O@sub 2@ reaction, catalyzed by nanosized Pt particles on alumina support. The resonant frequencies of the two QCMs, proportional to the total coverage of the reactants, were monitored. The time dependence of the frequency difference (proportional to the total coverage) reflects reaction kinetics on the Pt particles. These measurements are complemented by mass spectrometric measurements of the gas phase products, yielding wealthy information about reaction kinetics on a real catalyst at high pressure. In addition we also demonstrate the ability of the sensor for detection of kinetic phase transitions in the above reaction. The sensitivity of the sensor is estimated to about 30Hz/10@super 15@ Pt atoms. The noise level is < 1Hz thus enabling us to measure coverage changes corresponding to 2-3% ML.

SS-TuP26 Effect of Step Edges upon CO Dissociation over Ni Surfaces*, **H. Nakano**,* University of Tsukuba, Japan*; T. Fujitani,* National Institute for Resources and Environment, Japan*; J. Nakamura,* University of Tsukuba, Japan

We have studied the formation process of surface carbide on Ni(111) and Ni(977) by Boudouard reaction (2CO --> CO@sub 2, g@ + C@sub a@) using UHV-STM in order to clarify the dissociation site of CO. A reconstructed structure consisting of square units due to carbide was observed at the step-edges on Ni(111) when the carbide coverage was about @theta@ @sub c@ = 0.01. Islands of the reconstructed structure were formed on the upper terrace in the vicinity of specific step-edges. The same square units were then observed on the terrace at a carbide coverage of 0.13. This structure consisted of three domains in which one direction of the square unit corresponded to that of the Ni(111) substrate's hexagonal unit. Thus, the surface reconstruction caused by carbide formation was found to occur from step-edges. The formation rate of carbon on Ni(111) depended on annealing temperature after Ar ion sputtering. Increasing anneal temperature from 850 to 1100 K resulted in a decrease in formation rate of carbon by about 50 %. STM results showed that the number of defects on the Ni(111) surface decreased upon the annealing at 1100 K. These results indicate that Boudouard reaction or the CO dissociation occurs at defect sites. The formation rate of carbon on a stepped Ni(977) surface was promoted remarkably compared with Ni(111). The apparent activation energies of the carbon formation on Ni(977) and Ni(111) were measured to be - 36.4 and + 7.2 kJ/mol, respectively. It is considered that the formation of carbon consists of the CO dissociation at step sites and subsequent migration onto (111) terraces.

SS-TuP27 Ion Desorption from Molybdenum Oxide by Specific Core-to-Valence Resonant Excitations at the Mo L@sub 2,3@, Mo M@sub 2,3@ and O K-edges*, G. Wu, **Y. Baba**, I. Shimoyama, T. Sekiguchi,* Japan Atomic Energy Research Institute, Japan

Irradiation of X-rays on solid surface induces various chemical changes such as decomposition and desorption. Due to the localized nature of inner-shell electrons, the primary excitation localizes around specific element or specific chemical bond. The question is whether or not the primarily localized excitation leads to the specific chemical reaction. The examples for specific chemical-bond scission and ion desorption induced by core-level excitation have been reported for adsorbed molecules on solid surfaces. Here we present the results for the ion desorption from bulk material induced by a specific core-to-valence resonant excitation. Molybdenum trioxide was chosen as a sample, because this material is known to be sensitive to irradiation of X-ray or electrons. In the X-ray absorption near-edge structure (XANES) spectra, the resonance peaks corresponding to the excitations from Mo2p to 4d have two components due to the ligand-field splitting of 4d state, which are assigned as transitions from Mo 2p to triply degenerated t@sub 2g@-type orbits and doubly degenerated e@sub g@-type orbits. When we compare the desorption-yield curves with XANES spectra taken by total electron yield, the O@super +@ ion yield at the resonance from Mo 2p@sub 3/2@ into the e@sub g@-type orbits was enhanced compared to that into the t@sub 2g@-type orbits. Similar enhancements were also observed for the Mo M@sub 3@ and O K-edge excitations. Considering the antibonding character of the e@sub g@-type orbits, the enhancement of desorption is explained by the localization of excited electrons in the e@sub g@-type orbits which leads to the specific Mo-O bond breaking and O@super +@ desorption. The detailed mechanism will be presented on the basis of the results for the Auger decay spectra.

SS-TuP28 Surfactant Behaviors of Bi and As in the Growth of Ge/Si(001)-2x1 Systems Studied with Photoemission Spectroscopy*, **P. De Padova**,* Consiglio Nazionale delle Ricerche, Italy*; R. Larciprete,* ENEA, Italy*; C. Quaresima, A. Reginelli, S. Priori, E. Paparazzo, L. Moretto, P. Perfetti,* Consiglio Nazionale delle Ricerche, Italy

Heteroepitaxial Ge/Si(001)-2x1 systems show promising applications in the fabrication of infrared detectors. A layer-by-layer growth is essential for smooth films to be obtained, and this is greatly facilitated by addition of surfactant elements, such as As, Bi and Sb. Among these, Bi is a good candidate, as it little affects the Ge chemistry and has a low desorption temperature, whereas As has been generally regarded as being the ideal surfactant element. We used synchrotron radiation (SR) photoemission and XPS techniques to comparatively study the roles that Bi and As play in the growth of thin and thick Ge films on Si substrates. Angle-resolved SR core level spectra allowed us to identify two distinct growth modes in Ge/Bi/Si(001) systems as a function of Ge coverage. Sub-monolayer Ge coverages involve Ge- and Bi-atoms exchanging sites with each other, whereas greater Ge coverages involve the Ge-atoms lying both underneath Bi-atoms, as well as on top of the Si substrate. XPS depth-profiling conducted into a 15-monolayer Ge-film reveals that the Bi-atoms remain confined to the true surface. SR spectra of the Ge/As/Si(001) system show that the As-atoms lie anchored to the Si substrate, even for great Ge coverages, which is at striking variance with the expected layer-by-layer growth. Ge growth, carried out via codeposition of As and Ge on Si substrates, gives spectral evidences suggestive of the As atoms diffusing downward the Ge film, with no Ge-As site exchange taking place. We discuss our results in light of theoretical and experimental reports available in the literature, and propose an interpretation to account for the different surfactant behaviors of Bi and As.

SS-TuP29 Electron Transfer in Organic Monolayers*, **K. Raiber**, B. Zeysing, A. Terfort,* University of Hamburg, Germany

The electron transfer through organic monolayers is a field of research which is receiving an increased interest since these monolayers on conductive materials are not only used as barrier and protection materials@footnote 1,2@ but also as conductors. These new applications for the monolayers require a detailed understanding of the processes during the electron transfer through the monolayer. There are three different possible conduction mechanisms through monolayers discussed in literature:@footnote 3@ the through bond conduction, a through-bond tunneling and a through-space tunneling. To discriminate between the conduction and the tunneling mechanisms we investigated the electron transfer properties of unsubstituted aliphatic and aromatic molecules by cyclovoltammetry. To avoid problems with the match of Fermi-niveaus we attached an electrochemically active group to an aliphatic and an aromatic thiol, respectively, of approximately the same length and investigated the electron transfer within SAMs formed by these molecules on gold surfaces. The exact knowledge of the place of electron generation, which is determined by the immobilisation of the electrochemical active group on a gold electrode, allowed a better determination of the conduction mechanism. @FootnoteText@ @footnote 1@A. M. Becka, C. J. Miller; J. Phys. Chem. 1992, 96, 2657-2668. @footnote 2@ R. Haag, M. A. Rampi, R. E. Holmlin, G. M. Whitesides; J. Am. Chem. Soc. 1999, 121, 7895-7906. @footnote 3@K. Bandyopadhyay, K. Vijayamohanan, M. Venkataramanan, T. Pradeep; Langmuir 1999, 15, 5314-5322.

SS-TuP30 Reactions of Hydrazoic Acid (N@sub3@H) on Water and Gold Surfaces Characterized Using RAIRS and XPS*, S.R. Carlo, J. Torres, **D.H. Fairbrother**,* Johns Hopkins University

The chemistry of hydrazoic acid (N@sub3@H) on gold and amorphous ice surfaces was studied as a function of N@sub3@H exposure, temperature, and X-ray irradiation using reflection absorption infrared spectroscopy (RAIRS) and XPS. N@sub3@H adsorbed on ice at 100K initially led to azide production (N@sub3@@super-@), and subsequent N@sub3@H deposition. On Au, N@sub3@H adsorbed molecularly at 100K. On either surface annealing caused increased order in the film and loss of N@sub3@H correlated with N@sub3@@super-@ production. Three new IR bands were observed in the NH stretching region at T>180 K. The adsorption characteristics and thermal chemistry of N@sub3@H on ice suggest a chemisorbed state. These NH and N@sub3@@super-@ bands were stable to T>220K. Experiments were performed using N@sub3@D to elucidate the nature of these species. On both surfaces X-ray irradiation induced significant molecular desorption, increased azide concentration and production of the same three bands in the NH stretching region as observed when heating.

SS-TuP31 Adsorption and Desorption Processes of Alkanethiol Self-Assembled Monolayers on Au(111)*, **J. Noh,*** Frontier Research System, RIKEN, Japan*; T. Araki,* Saitama University, Japan*; K. Nakajima, M. Hara,* Frontier Research System, RIKEN, Japan

Adsorption and desorption processes of alkanethiol self-assembled monolayers (SAMs) on Au(111) have been examined by scanning tunneling microscopy (STM) and thermal desorption spectroscopy (TDS). New intermediate phases that are expected by a recent diffraction study from coverage-dependant SAMs prepared by a wet process were observed in a molecular level, revealing phase transitions from the striped phase to the upright phase. In addition, surface structure and molecular species desorbing from such SAM samples as a function of surface temperature were monitored by TDS and STM. TDS spectra for dimer molecules as well as alkyl groups formed after cleavage of C-S bond clearly show second-order desorption behavior implying the associative desorption of alkanethiolate adsorbed on Au(111) surface. STM images clearly show structural transitions due to desorption of molecules at elevated surface temperature. Moreover desorption process and stability of pre-covered alkanethiol SAMs in pure solvents at room temperature were investigated. In this study, it is revealed that desorption of alkanethiol SAMs under solvent and UHV conditions initiate at domain boundaries and near depressions that have weaker lateral interactions compared to close-packed domains, followed by desorption of molecules in close-packed domains. From these results, we discuss the adsorption states in alkanethiol SAMs as well as the precise model of the adsorption and desorption processes.

SS-TuP32 Hydroxymethylcyclopropane on Oxygen-covered Mo(110): A Radical Clock on a Metal Surface?*, **I. Kretzschmar**, J.A. Levinson, C.M. Friend,* Harvard University

Radical clocks are a well-established means for the determination of radical lifetimes in liquid and gas-phase organic chemistry.@footnote 1@ However, no equivalent tools yet exist for the evaluation of radical lifetimes on surfaces, although radicals are often proposed as the most important intermediates in surface reactions. In this study, the reaction of hydroxymethylcyclopropane has been investigated on clean and oxygen-covered Mo(110) surfaces. Since methylcyclopropane is the expected product upon C-O bond scission in hydroxymethylcyclopropane and represents the smallest possible model system for a radical clock, this molecule seems to be a promising system for gauging radical lifetimes in the vicinity of the surface. Changes in binding and structure of the adsorbate are monitored using a combination of temperature programmed reaction spectrometry and reflectance-infrared absorbance spectroscopy. These studies reveal that the surface species formed upon adsorption of hydroxymethylcyclopropane onto oxygen-covered Mo(110) is stable up to 400 K. Above 450 K, 1-butene, 1,3-butadiene, and ethene are produced. In addition, two new vibrational peaks develop at 1245 cm@super -1@ and 1645 cm@super -1@ in the infrared spectra obtained after heating to 450 K. Both peaks are attributed to ring-opened surface intermediates: the 1645 cm@super -1@ peak to alkoxide species and the 1245 cm@super -1@ peak to the formation of a metal-bound alkyl species after ring opening. The observation of ring-opened products points to the fact that ring opening is faster than hydrogen abstraction from the surface. The experiments are discussed in the general framework of alkyl oxidation processes. @FootnoteText@ @footnote 1@ See for example: Newcomb, M. Tetrahedron, 1993, 49, 1151.

SS-TuP33 LEED and STM Investigations of the Heteroepitaxy of Perylenetetracarboxylic-dianhydride (PTCDA) on Hexa-peri-benzocoronene (HBC) on Reconstructed Au(111) Surfaces*, T. Fritz, **F. Sellam**, T. Schmitz-Huebsch, M. Toerker, S. Mannsfeld, H. Proehl, K. Leo,* TU Dresden, Institut fuer Angewandte Photophysik, Germany

The fabrication of multilayered films and superlattices consisting of different molecules has recently attracted considerable interest because of the prospective applications of those structures as active optoelectronic components in modern integrated devices. While the epitaxy of inorganic semiconductor heterojunctions is already well established, only little is known about the growth of organic heterostructures. We present the result of the combination of two OMBE (organic molecular beam epitaxy) grown materials of planar molecules, namely perylene-tetracarboxylic-dianhydride (PTCDA) and hexa-peri-benzocoronene (HBC). As substrate the Au(111) surface was chosen. Two complementary surface analysis methods which are low energy electron diffraction (LEED) and scanning tunneling microscopy (STM) have been applied to characterize the growth of the ultrathin organic molecular heterojunction and to determine the epitaxial relation between the two lattices. In a first step, we investigated the growth of HBC on reconstructed Au(111) surfaces. Large domains which are defect free on the molecular scale are observed by STM. The LEED investigations reveal that HBC grows on reconstructed Au(111) in a commensurate hexagonal structure. The HBC lattice is rotated by 30° with respect to the Au[110] direction and therefore it appears only in a single domain orientation. In a second step, a monolayer of PTCDA was deposited on HBC and structurally characterized. The LEED and STM measurements show the well-known herringbone alignment of the PTCDA molecules, similar to that in the (102) bulk plane with two molecules in a rectangular unit cell, indicating the p2gg space symmetry group. Besides these findings, the pronounced two-dimensional Moiré pattern in the STM images was used to determine the relative orientation of the PTCDA unit cell with respect to the underlying HBC lattice, revealing a parallel orientation between the short PTCDA lattice vector and the HBC[10] direction.

SS-TuP34 DeNOx Reactions on MgO(100): Photoemission and Density Functional Studies*, **T. Jirsak**, J.Z. Larese,* Brookhaven National Laboratory*; A. Maiti,* Molecular Simulations Inc.*; J.A. Rodriguez,* Brookhaven National Laboratory

In environmental catalysis the destruction or removal of nitrogen oxides (DeNOx process) is receiving a lot of attention. Nitrogen oxides (NO and NO@sub 2@) are formed in automotive engines and industrial combustion systems. Metal oxides can be useful in the control of environmental pollution. It has been found that MgO has the ability of trapping the NO@sub 2@ formed in automotive engines during the burning of fuels under oxygen-rich conditions. Synchrotron-based photoemission and first-principles density-functional calculations (DF-GGA) have been used to study the chemistry of NO and NO@sub 2@ on MgO(100). NO is weakly adsorbed on the oxide surface. On flat MgO(100), DF results predict an NO adsorption energy of 6 kcal/mol, which is close to the value of 5 kcal/mol observed experimentally. At steps of the surface, NO interacts with tetra- and penta-coordinated Mg atoms and the adsorption energy can increase to 9 kcal/mol. On MgO@sub 1-x@, O vacancies and defect sites enhance the bonding energy of NO, and lead to the production of N@sub 2@O at 100 K plus the deposition of N above 200 K. NO@sub 2@ is very reactive on terraces and steps of MgO(100). Adsorbed NO@sub 3@ and NO@sub 2@ are detected after exposing the oxide to NO@sub 2@ at 150 K. Strong bonding interactions between Mg sites and NO@sub 3@ favor disproportionation of adsorbed NO@sub 2@. The large differences in the reactivity of NO and NO@sub 2@ reflect the fact that nitrogen dioxide is a much better electron acceptor. The role of metal promoters (K,Cs,Cr,Ni) on DeNOx operations on MgO will be discussed.

SS-TuP35 Oxygen Loss and Recovering Induced by Ultra High Vacuum and Oxygen Annealing on WO3 Thin Film Surfaces*, M. Pssacantando, L. Lozzi, C. Cantalini, **S. Santucci,*** University of L'Aquila, Italy

Thin films of WO3 with thickness in the range of 150 nm have been deposited onto silicon substrates by thermal evaporation. The films as deposited and annealed at 300 and 500°C in oxygen for 24 hours were submitted to UHV annealing. XPS measurements (W4f and valence band) show for the as deposited sample annealed at 200°C in steps of 50°C a marked increase of the metallic features of the surface attributable to oxygen loss. This film extracted from the UHV ambient and annealed in oxygen at 200° shows XPS features meaningful of a renewed oxygen incorporation which is again reduced by the UHV annealing demonstrating an evident reversibility towards the oxygen loss and recovery for this kind of sample. Also the WO3 film treated by oxygen annealing at 300° shows an increase of the metallic character of the film surface due to oxygen loss as a consequence of the UHV annealing up to 300°C but the sample extracted from the UHV ambient and submitted to a second annealing in oxygen at 300°C for 24 h recovers oxygen remaining substantially stable and scarcely influenced by successive UHV annealing. Finally the surface of the sample initially annealed in oxygen at 500°C appears at the XPS measurements evidently stable after the UHV annealing up to 500°C. These results have been confirmed by Scanning Tunneling Microscopy measurements which evidenced for the as deposited sample a narrowing of the band gap when the annealing temperature in UHV overcomes 300°C. Gas sensing towards NO2 of samples with UHV annealing modified surfaces have been also investigated giving encouraging results respect to the increase of the sensitivity of the sensor.

SS-TuP36 Spectral Changes in Far and Near Field Optical Microscopy of Surface Clusters*, **M. Xiao,*** CCMC-UNAM

We theoretically study the spectra in far and near field optical microscopy of a group of nanoscopic scatterers such metallic and semiconductor quantum dots two-dimensionally distributed on a plane surface. Our emphasis is on the spectral changes in the far and near field spectra as compared with spectra of individual scatterers. We show that extra spectral changes can be observed when the coupling between scatterers becomes strong. If the coupling is mainly due to the evanescent field, the produced spectral changes are localized in the near field zone. The extra spectral changes include both red and blue shift, as well as deformation.

SS-TuP37 1-to-9 keV Electron-Induced Surface Chemistry in Ultra High Vacuum Systems*, Q. Ma,* Argonne National Laboratory, US*; R.A. Rosenberg,* Argonne National Laboratory

Electrons in accelerators are ubiquitous. They range in energies from MeV down to a few eV (secondary electrons). Collisions of these electrons with surfaces of accelerator components may produce reactions that will modify the properties of the surface/vacuum interface. In order to gain insight into these reactions, we have studied the interaction of 1-to-9 keV electrons with the Ar-ion sputtered surfaces of Al, TiN, and Si, under ultra high vacuum conditions using scanning Auger electron spectroscopy. Electron-induced surface chemistry takes place on all these surfaces. For both Al and Si, layer-by-layer growth of oxides was produced by electron beam bombardment. In the case of Al, a clear threshold behavior of the oxidation rate is observed for excitation energies near the Al K-core hole (1560 eV), which suggests participation of secondary electrons in the surface reaction. In the case of TiN films, surface carbonation occurred with 9 keV electron bombardment while no reaction was observed with 5 keV el ectrons. No enhancement of the surface oxidation rate was observed. It will also be shown that the deposited carbonaceous layer is graphitic in nature, resulting in a decrease of the secondary electron yield and thus an increase of the observed sample current. This work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences under Contract No. W-31-109-ENG-38.

Thin Films
Room Exhibit Hall C & D - Session TF-TuP
Poster Session

TF-TuP1 Influence of Annealing Temperature on Simultaneous Vapor Deposited Calcium Phosphate Thin Films*, M. Hamdi,* *A.M. Ektessabi,* Kyoto University, Japan

Calcium phosphate is an important bioceramic with tremendous potential for biomedical applications. Its unique bioactivity promotes rapid bone growth and strong interfacial fixation that has particular benefit to orthopedic and dental applications. The effect of different annealing temperature on the characteristics of thin film calcium phosphate coatings fabricated by a novel simultaneous vapor deposition method was investigated. Heat treating the as-deposited films was necessary to change the amorphous coating to a crystalline coating. The films were annealed for 3 h at 400, 700, 1000 and 1200°C in air. After annealing, the structure and the chemical composition of these films were characterized with incident light microscopy, rutherford backscattering spectroscopy and x-ray diffraction. Scratch test was conducted to measure the adhesion strength of the coatings to the substrate. Results showed that after annealing at 1000°C, crystalline hydroxyapatite appeared to co-exist with tricalcium phosphate phase. The surface roughness increased with increasing annealing temperature. The adhesion of the coatings was highly affected by the annealing temperature. From the results, it can be suggested that 1000-1200°C is probably the best annealing temperature range for calcium phosphate coatings produced by simultaneous vapor deposition method.

TF-TuP3 Formation and Evolution of Photoluminescence Si-based Nanostructured Thin Films Prepared by Laser Ablation*, A. Kabashin,* *M. Meunier,* Ecole Polytechnique de Montreal, Canada*; R. Leonelli,* University of Montreal, Canada

A method of Pulsed Laser Ablation (PLA) from a Si target in an inert He ambient has been applied in combination with different post-deposition oxidation procedures for the fabrication of Si/SiOx nanostructured films on Si substrates. The films exhibited strong visible photoluminescence (PL), which remained stable even under a prolonged continuous irradiation of the sample by an excitation laser light. The peak energy of the PL spectra could be finely varied between 1.58 and 2.15 eV by a change in the residual gas pressure during the deposition process. An effect of thermal annealing on the PL properties of the Si/SiOx films has been examined and compared with the results for Si-based films produced by thermal evaporation from a Si target in vacuum. For both deposition techniques, the thermal annealing led to a dramatic change of PL properties giving rise to a fixed PL peak around 2.2 eV. Photoluminescent properties of particles formed by PLA with natural oxidation were different than those of thermally oxidized amorphous Si films. In addition, the PL properties of the as-deposited films were found to be sensitive to surface chemistry reactions. A change of storage ambient and oxidation conditions could lead to significant changes of positions and intensities of PL peaks. Possible mechanisms of formation and evolution of PL are considered.

TF-TuP4 Deposition of Device Quality Amorphous Silicon, a-Si:H, Thin Films by the Hollow Cathode Plasma-Jet Reactive Sputtering System*, Z. Hubicka,* ***R.J. Soukup****, G.K. Pribil, N.J. Ianno,* University of Nebraska, Lincoln

Device quality hydrogenated amorphous silicon, a-Si:H, thin films have been deposited by means of a dc hollow cathode plasma jet with magnetic field confinement. Single crystal silicon nozzles have been reactively sputtered in the high density hollow cathode discharge. Only nontoxic gases argon and hydrogen have been used for this purpose. Different configurations of the dc hollow cathode have been used for the deposition process. Device quality a-Si:H thin films have been achieved with light to dark conductivity ratios >10@super 6@ and with the light conductivity near 10@super -5@ S and dark conductivity between 10@super -11@ and 10@super -12@ S. This was accomplished with a specific configuration of the hollow cathode discharge in the silicon nozzle. Our best films have a Tauc-band gap near 1.8 eV and an atomic hydrogen concentration of about 14%. The growth rate achieved for device quality a-Si:H films was in the range of 2 to 3 µm/h.

TF-TuP5 Influence of Bias Voltages on the Oxygen Diffusion Behaviour in dc Magnetron Sputtered In/Sn Films*, M. Quaas, H. Wulff,* ***H. Steffen****, R. Hippler,* University of Greifswald, Germany

Thin metallic In/Sn films were deposited on unheated Si(100) wafers by means of dc planar magnetron sputtering at different negative substrate voltages. The In/Sn x-ray reflection line profiles of these films are broadened. The broadened profiles can be considered as an indicator of decreasing lattice perfection in the as-deposited films. To study the influence of the different microstructures on the oxygen diffusion behaviour these films were annealed in a vacuum chamber mounted on a theta-theta-diffractometer. Using in-situ high-temperature grazing incidence x-ray diffractometry (GIXRD) the growth of crystalline indium-tin-oxide (ITO) layers was observed. From the time dependence of the ITO(222) peak intensity conclusions on the reaction kinetics can be drawn. An analytical model was developed for the investigation of the diffusion process by means of the x-ray integral intensity. From this model the effective diffusion coefficients D were determined for films deposited at different substrate voltages. The correllation between the film microstructure and the variing diffusion coefficients is discussed.

TF-TuP6 Study on Indium Nitride Films Deposited by DC Magnetron Sputtering*, P.K. Song*, *D. Sato, N. Ito, Y. Shigesato,* Aoyama Gakuin University, Japan

The III-V nitride semiconductors with a wurtzite structure such as aluminum nitride (AlN), gallium nitride (GaN), indium nitride (InN), have been investigated for various applications including optoelectronic devices because they have direct energy band gaps corresponding to wide wavelengths from the red to the ultraviolet. However, InN has received little attention compared with AlN or GaN, because its poor thermal stability and difficulties in depositions. In this study, InN films were successfully deposited on soda-lime glass at the substrate temperature T@sub s@=RT-400ï½°C by dc reactive magnetron sputtering using In metal target under various total gas pressure (P@sub tot@=0.5-3.0Pa) of mixture gases of Ar and N@sub 2@. Crystal structure and surface morphology of the films were investigated by X-ray diffraction (XRD) and atomic force microscope (AFM). Without substrate heating, a clear InN (002) XRD peak was observed for the films deposited at 0.5-3.0 Pa with N@sub 2@ gas flow ratio higher than 60%. With increasing P@sub tot@ from 0.5 to 3.0 Pa, degradation in the crystallinity of the films was clearly observed. Based on these results, two possible mechanisms are postulated. One is that the chemically active species generate by electron-impact dissociation of N@sub 2@ molecules could be increased with the decreasing P@sub tot@ and increasing electron temperature, which should result in the enhancement of the crystallization during reactive film growth. Another mechanism is that the crystallinity of the film is affected by the kinetic energy of sputtered In atoms arriving at substrate surface which could enhance surface migration of the In atoms and hence the crystallinity. The effects of increasing T@sub s@ on the film structure will also be discussed in detail.

TF-TuP7 The Effect of Heat-treatment on the Structural and Mechanical Properties of MoS@sub 2@/Ti Composite Coatings*, B.J. Kim,* *J.H. Dautzenberg,* Eindhoven University of Technology, The Netherlands

MoS@sub 2@/Ti composite coatings have been coated on stainless steel by dc magnetron sputtering. After deposition, MoS@sub 2@/Ti coatings were heat-treated in vacuum in order to investigate the effect of heat treatment on the mechanical properties of the coating. Before and after heat treatment, the structure and concentration of co-sputtered MoS@sub 2@/Ti coating were analyzed by x-ray diffraction method, energy disperse spectroscopy, as well as x-ray photoelectron spectroscopy. The mechanical properties of the coatings such as hardness, elastic modulus, residual stress, and critical fracture strain of bending, were also measured by nano-indentation method, thin foil method, and bending test with electro-chemical detection. Ti addition to MoS@sub 2@ coating prohibits the micro- or macro-crystallized structure of the coating, and MoS@sub 2@/Ti coating makes a single-phase solid solution structure up to 20 at% Ti. Mechanical properties of coating are dependent on Ti concentration. The hardness and elastic modulus of MoS@sub 2@/Ti composite coatings increased as increasing Ti concentration. The residual stresses of MoS@sub 2@/Ti composite coatings dramatically increased by adding Ti to MoS@sub 2@ coating. MoS@sub 2@/Ti composite coatings were micro- or macro-crystallized if the heat treatment temperature was higher than 500°C. It resulted in the increase of porosity and decrease of hardness of the coating. The concentration of sulfur abruptly decreased, if the heat treatment temperature is higher than 750°C.

TF-TuP8 Supermagnetron Plasma CVD and Qualitative Analysis of Electrical Conductive Hard Carbon (DLC) Films*, H. Kinoshita,* *M. Yoshida,* Shizuoka University, Japan

Using a supermagnetron plasma chemical vapor deposition (CVD) method, electrical conductive diamond-like carbon (DLC) films were formed.@footnote 1@ The electrical conductive DLC films were suited for the formation of high performance field emitters, which were formed by coating Si tips with them. In the formation of DLC films on Si and glass wafers, i-C@sub 4@H@sub 10@/N@sub 2@ mixed gases were introduced into the discharge chamber. Deposition rate, hardness and resistivity were measured as a function of N@sub 2@ concentration, total gas pressure, rf powers or temperature of lower-electrode on which a wafer was put. With increase of N@sub 2@ concentration (up to 70%), rf powers and lower-electrode temperature, the film resisitivity was decreased. And also with decrease of total gas pressure, the film resisitivity was decreased. FT-IR spectroscopy measurements revealed that the increase in electrical conductivity could be attributed to CN single and triple bonds creation in DLC films. The lowest resistivity of 0.034 @ohm@ cm was achieved at the N@sub 2@ concentration of 65%, total gas pressure of 30mTorr, upper- and lower-electrode rf powers of 1kW/1kW, and lower-electrode temperature of 100 °C. @FootnoteText@@footnote 1@H.Kinoshita and A.Yamauchi, J.Vac.Sci.Technol.A 14, 1933 (1996).

TF-TuP9 Deposition of W Films using Different Underlayers*, L.V. Kozlovsky, A. Antinsh,* ***V. Pashkevich,*** University of Daugavpils, Latvia

It is known that the formation of beta-Ta crystalline phase in sputtered Ta films depends on the nature of the substrate or underlayer. Comparison of our data as well as of results of various authors reveals the correlation between beta-Ta formation in Ta/Me bilayers and mismatching of the shortest interatomic distances (SID) in bcc Ta and in Me. Beta-Ta phase presents in the Ta films when SID mismatching greater of 9%. The aim of the present work was to determine whether beta-W formation in W/Me bilayers occurs at such conditions. We deposited 100 nm Me/X nm W (Me: Nb,Al, Fe, Zr, Hf, Dy ; X = 20,50, 100, 200 nm) bilayers on near room-temperature glass substrates in a Xe discharge at a pressure of (7 - 9) x10@super -4@ Torr using Penning discharge sputtering devices. The base pressure was nearly 5x10@super -9@ Torr.10 nm C underlayer was deposited on substrates at the same vacuum conditions before bilayers deposition. The structure of the films was investigated by X-ray diffraction (XRD). In the case of Nb and Al the SID mismatching is less of 4% but for other metals it is in the interval (10 - 28)%. Wolfram layers structure was characterized as bcc W. XRD profiles for all bilayers had no peaks corresponding to beta-W. W films on Nb and Fe had texture (110). Preferred orientation of {110} and {211} planes parallel to the substrate plane was found in W layers in the case of Al, Zr, Hf, Dy underlayers. The results of present work have shown that beta-W formation in Me/W bilayers is not dependent on underlayer. Data of the bilayers crystal structure investigations will be presented and discussed.

TF-TuP10 Energetic Oxygen Ions in the Reactive Sputtering of Zr Target in Ar+O@sub 2@ Atmosphere*, K. Tominaga,* ***T. Kikuma,*** University of Tokushima, Japan

In the sputtering of Zr target in Ar+O@sub 2@ atmosphere, ZrO@sub 2@ films are deposited. However, sometimes anomalous phenomena that the films are easily peeled from the substrate or degraded. These seems to be due to the presence of the energetic oxygen ions which are generated in the sputtering. Therefore it becomes important to know the extent of the flux of energetic oxygen ions. We constructed a probe to estimate the flux of energetic oxygen ions and applied it to the observation of the energetic oxygen ions in the reactive sputtering of Zr. At the same time, we observed the photoemission intensity from the sputtered Zr atoms, monitoring the target surface oxidization. The results show that the Zr target is very active in oxygen atmosphere and oxydized fully with a small oxygen partial pressure. The flux of energetic oxygen ions increases with increasing the oxidized area of the target. The flux of energetic oxygen ions for Zr target is 2 or 3 times stronger than that for Zn target. This is thought to be due to the thick oxygen layers on the Zr target.

TF-TuP11 Low Temperature Crystallization of TiO@sub 2@ Thin Films Sputter-deposited in Ar-H@sub 2@O Plasma*,* ***T. Ohwaki,*** *Y. Taga,* TOYOTA Central R&D Labs., Inc., Japan

Polycrystalline TiO@sub 2@ thin films are widely used as photocatalytic materials. Low temperature crystallization of the films is one of the important techniques for realizing wide spread application. We studied low temperature process for preparing TiO@sub 2@ thin films by sputtering. We found that the TiO@sub 2@ thin films deposited by reactive magnetron sputtering of Argon-water plasma were crystallized to anatase poly-crystal by post-annealing at only 200°C in air, while TiO@sub 2@ thin films sputter-deposited by Argon-oxygen plasma were crystallized at above 500°C post-annealing. To clarify the mechanism of low temperature crystallization, we investigated the structure of TiO@sub 2@ thin films sputter-deposited by Ar-D@sub 2@O or Ar-O@sub 2@ plasma by means of Infrared-Reflection Absorption Spectroscopy (IR-RAS). The detailed analyses of the absorption bands revealed an existence of hydroxyl groups in TiO@sub 2@ thin films sputter-deposited by Ar-D@sub 2@O plasma and relaxation of the lattice. This result suggests that the introduced hydroxyl groups cut the amorphous network structure of the TiO@sub 2@ thin films, which enhances the rearrangement of the atoms in the films by post-annealing.

TF-TuP12 Selective Growth of TiO@sub 2@ Thin Films on Si(100) Surfaces by Combination of MOCVD and Microcontact Printing Method*, B.-C. Kang, J.-H. Lee,* ***H.-Y. Chae,*** *D.-Y. Jung, S.-B. Lee, J.-H. Boo,* Sungkyunkwan University, Korea

Patterning of TiO@sub 2@ thin films was successfully performed by MOCVD onto Si (100) substrates of which surface were modified by an organic thin film. The organic thin film of self-assembled monolayer (SAM) was in first obtained by the micro-contact printing (µm-CP) method. Selective deposition of TiO@sub 2@ thin film with 1500 Å thickness has then been carried out onto those surfaces at the temperature in the range of 300 to 500 °C by MOCVD without any carrier and bubbler gas. AES and XRD analysis showed that deposited TiO@sub 2@ thin film has a stoichiometric composition in the depth and polycrystalline anatase phase. @alpha@-step profile and optical microscopic images also showed that the boundaries between OTS SAMs areas and selectively deposited TiO@sub 2@ thin film areas are very definite and sharp. Capacitance-voltage measurement made on a TiO@sub 2@ thin film gave a dielectric constant of 21, suggesting a possibility of electronic materials applications.

TF-TuP13 Oxidation Kinetics of the Growth of Thin Alumina formed by Plasma Oxidation*,* ***A. Quade,*** *H. Wulff,* University of Greifswald, Germany

Plasma treatment is an original way to modify the surface of metals and to improve their properties for an application in industry. In our study thin Al films were plasma oxidized using a 2.45 GHz slot antenna microwave plasma source (SLAN) at different types of chemical reactive and non-reactive plasma species to form thin aluminium oxide films. To determine the activation energy for plasma oxidation process investigations at different substrate temperatures were performed. For the characterization of the Al and the developed oxide grazing incidence x-ray reflectometry (GIXR), grazing incidence x-ray diffractometry (GIXRD), Fourier-Transform infrared spectroscopy (FT-IR) and x-ray photoelectron spectroscopy (XPS) were used. Because the formed alumina is x-ray amorphous, the integral intensity of Al(111) peak of the non-reacted Al film was determined time-controlled for the quantification of the developed oxide. Together with the total thickness of the layer these values allow the calculation of significant kinetic parameters. The alumina film growth is controlled by two rival processes, a diffusion process and a sputter process. The growth kinetics depends on plasma type, concentration of activated oxygen species and temperature.

TF-TuP14 Epitaxial Growth of CeO@sub 2@ Film on YSZ Buffered Si (111) Substrates*, J.H. Yang*, *K.W. Lee, J.W. Seo, C.Y. Park,* Sungkyunkwan University, Korea

We have grown cerium dioxide (CeO@sub 2@) films as an insulating layer for silicon-on-insulator (SOI) structure. When CeO@sub 2@ was deposited on Si (111) substrate up to 620 by using electron beam evaporator (ANELVA VI-43N), at the interface between CeO@sub 2@ film and Si (111) substrates, the SiO@sub 2@ layer was observed which is in agreement with earlier report.@footnote 1@ The structure of CeO@sub 2@ films on Si (111) substrate was formed to be columnar. We observed that the columnar structure of CeO@sub 2@ films and SiO@sub 2@ formation disturbed the epitaxial growth of the Si film on top layer. Hence, we have deposited YSZ as a buffer layer on the Si (111) substrate and grown CeO@sub 2@ film. We analyzed YSZ and CeO@sub 2@ films by XRD, HRTEM and AFM. We found that deposition of YSZ on Si (111) prohibits the growth of SiO@sub 2@ layer. The morphology of CeO@sub 2@ film on YSZ buffered substrates was improved as compare with the morphology of CeO@sub 2@ film with not YSZ buffered substrates. @FootnoteText@ @footnote 1@C.G. Kim et al, J. Kor. Phys. Soc., 32, 64(1998).

TF-TuP15 The Effect of Annealing on the Electroless Plated Cu Metallization for Sub-micron Interconnection*, J.H. Lin,* National Tsing Hua University, Taiwan, Taiwan, ROC*; T.L. Lee,* National Chiao Tung University, Taiwan, TAIWAN, ROC*; Y.Y. Tsai,* National Tsing Hua University, Taiwan, TAIWAN, ROC*; X.W. Liu,* National Tsing Hua University, Taiwan, Taiwan,ROC*; C.C. Lin,* National Chiao Tung University, Taiwan, TAIWAN, ROC*; H.C. Shih,* National Tsing Hua University, Taiwan, Taiwan,ROC

Both patterned and blank wafers are carried out using Pd as catalyst by plasma immersion ion implantation (PIII) after which Cu is electroless plated. The characteristics of electroless plated copper specimens after annealing in the 95% nitrogen + 5% hydrogen ambient atmosphere with an annealing temperature from 150 to 700 for 1 hour are investigated by sheet resistance, surface roughness, crystallographic texture, cross-section morphology, film hardness, adhesion strength and microstructure. The sheet resistivity of Cu film decreases from 3.8 to 3.3 µ *-cm after annealing at the temperature from 150 to 700. AFM shows that the surface became rougher as the annealing temperature getting higher. HRTEM images show that, the Pd implantation layer of the as-received specimen is an amorphous structure and crystallized after the annealing treatment. If the annealing temperature is higher than 300, the copper reflow effect in via or trench is very clear. Therefore, the post electroless copper annealing at about 300 stabilizes the copper microstructure and completes interconnect metallization performance.

TF-TuP16 SrBi@sub 2@Ta@sub 2@O@sub 9@ Ferroelectric Films Deposited by PLD Under Different Annealing Conditions*, M.P. Cruz,* Centro de Investigacion y de Estudios Superiores de Ensenada, México*; J.J. Portelles,* Universidad de La Habana, Cuba*; J.M. Siqueiros,* UNAM, México

A new step in the deposition process of SrBi@sub 2@Ta@sub 2@O@sub 9@ (SBT) films is introduced to avoid short circuits in the electrode-ferroelectric-electrode capacitor due to microcracks in the SBT material. Here, the SrBi@sub 2@Ta@sub 2@O@sub 9@ films, deposited on Pt/TiO@sub 2@/SiO@sub 2@/Si substrates by PLD, were grown in a two-step process, each with its corresponding annealing treatment, in such a way that the second deposit fills the cracks of the first layer preventing the percolation of the electrode material from the top to the bottom electrode. SEM, TEM, XRD and AES techniques were used to characterize the films. X-ray analysis showed a BiO@sub 2@ crystalline phase for low deposition and annealing temperatures and its transformation into polycrystalline SBT as those temperatures increased. After Pt top electrodes were deposited on the SBT films, the micro structural results obtained with the abovementioned techniques, were correlated to the ferroelectric properties observing an increase in polarization values with processing temperature. DGAPA-UNAM, Proj. IN104000, CoNaCyT, Proj. 33856E. Thanks are due to E. Aparicio, P. Bartolo, J. Fernández, I. Gradilla, P. Ruiz and G. Vilchis.

TF-TuP17 Effect of Pulsing in Dual-mode Microwave/Radio Frequency Plasma on the Growth of SiN@sub 1.3@ Optical and Protective Coatings*, R. Vernhes,* *O. Zabeida, J.E. Klemberg-Sapieha, L. Martinu,* Ecole Polytechnique of Montreal, Canada

Plasma enhanced chemical vapor deposition (PECVD) is becoming increasingly attractive for the fabrication of optical films and coatings. The main reason is a possibility to obtain suitable optical, mechanical, permeation barrier and other functional characteristics when depositing on temperature-sensitive substrates such as polymers. In the present work, we deposited amorphous hydrogenated silicon nitride (SiN@sub 1.3@) in dual-mode microwave/radio frequency (MW/rf, 2.45 GHz / 13.56 MHz) discharge using a silane - ammonia mixture. We systematically studied the effect of MW and rf power modulation, namely the effect of pulsing frequency, duty cycle, and pulse synchronization on the optical (refractive index, extinction coefficient), mechanical (stress, microhardness, adhesion, etc.) and microstructural characteristics (concentration of hydrogen, chemical bonding, sutface morphology etc.). Using time- and mass-resolved ion energy analysis, we determined the effect of dissipated power and self-bias potential on the instantaneous ion energy distribution functions and on the energetics of the film growth. We found that, depending on rf matching, two distinct modes of operating the pulsed MW/rf discharge are possible, namely (i) when rf power is delivered during MW pulse, and (ii) when it is delivered between MW pulses. We discuss the possibilities to match in one design the optical and mechanical properties necessary to obtain enhanced film system stability for advanced optical and optoelectronic applications.

TF-TuP18 Synthesis of Cubic Boron Nitride Films on Ion Implanted Silicon Substrates*, Q. Li*, *Z.F. Zhou, I. Bello, C.S. Lee, S.T. Lee,* City University of Hong Kong, China

Cubic boron nitride (c-BN) films were prepared by radiofrequency (rf) magnetron sputtering of a hexagonal boron nitride (h-BN) target in Ar/N@sub2@ mixtures. The boron nitride films were deposited on chemically cleaned and in-situ presputtered silicon substrates. The substrates were implanted by boron, nitrogen and nickel ions and their combinations. During deposition, the substrates were pulsed biased and heated to 600 °C. The synthesized c-BN films showed good adherence to the substrate and exhibited phase purity over 90 % as determined by fourier transform infrared spectroscopy (FTIR). Atomic scale analysis, using high resolution transmission electron microscopy (HRTEM), showed nanocrystalline boron nitride structure. Cubic boron nitride phase grew both on the silicon substrates directly and the top of transition h-BN layers. The presented c-BN synthesis reduced the film stress as indicated by the beam bending technique and shift of the absorption peak of TO mode in FTIR spectra. The implanted species acted as active sites for film/substrate interfacial reaction and contributed to the stress reduction. The experimental results showed that the film stress was tailored by the presented novel method established on interfacial engineering which in return yielded high quality c-BN films.

TF-TuP19 Preparation and Characterization of Amorphous CN@sub x@ Thin Films by Pulsed Laser Deposition*, Y. Aoi*, *K. Ono, K. Sakurada, E. Kamijo,* Ryukoku University, Japan*; M. Sasaki, K. Sakayama,* Industrial Research Center of Shiga Prefecture, Japan

Compounds in carbon-nitrogen system are interesting because they exhibit unique properties such as high value of hardness, low friction coefficient, chemical inertness, and variable elctronic and optical properties. In this paper, amorphous carbon nitride (a-CN@sub x@) thin films were deposited on a Si substrate by pulsed laser deposition (PLD) by use of graphite target under various deposition conditions. We have investigated the bonding structure of deposited films. Structural changes by heat treatment were also investigated. The PLD system used in this study consists of a KrF excimer laser, nitrogen radical beam source, and vacum chamber. The laser beam was focused onto a rotating graphite target surface to give various energy density. Deposition was carried out in N@sub 2@ atmosphere, in Nitrogen plasma, and under irradiation of nitrogen radical beam. Heat treatment of films were carried out following to the deposition in the vacuum chamber. The films were charactereized by XPS, FT-IR, Raman spectroscopy, and TEM observation. The maximum N/C ratio of the deposited film was 0.24 in the present experimental conditions. N 1s electron spectra of deposited films indicated the nitrogen atoms in the film were mainly bonded to sp@super 2@ and sp@super 3@ hybridized carbon atoms. FT-IR and Raman spectra indicated that N-spC are small as compared with N-sp@super 2@C and N-sp@super 3@C. The fraction of N-sp@super 3@C increased with increasing N/C ratio in the deposited film. The heat treatment induced a nitrogen loss and graphitization of the film. It was found that nitrogen atoms bonded to sp@super 3@C are preferentially eliminated by heat treatment.

TF-TuP20 Sputtered Aluminum Nitride Thin Films for Bulk Acoustic Wave Resonators*, **R.N. Tait**,* Carleton University, Canada

Thin film bulk acoustic resonators formed by sputter deposition of piezoelectric films of aluminum nitride on silicon substrates offer an attractive approach to monolithic integration of high Q passive circuit elements with active devices. Such resonators could provide low cost, high performance filters for the steadily growing numbers of consumer wireless communication devices. Fabrication of these resonators requires a well characterized low temperature deposition process for aluminum nitride. This material has been studied for use in sensors and actuators, as well as acoustic wave devices. Radio frequency reactive magnetron sputtering produces high quality films. The deposition rate is too slow to be practical for many applications, however for high frequency resonators operating above 1 GHz the film thickness and deposition time is more reasonable. This work describes aluminum nitride films deposited by radio frequency reactive magnetron sputtering, using a Box-Behnken experimental design. Factors included power from 2 to 6 W/cm@super 2@, pressure from 1 to 1.6 Pa, and N@sub 2@ flow from 50% to 100% of the total flow. Measured results include X-ray diffraction spectra and measurements of piezoelectric coefficients. X-ray diffraction measurements indicate highly (002) c-axis oriented films. Piezoelectric coefficients were measured by depositing aluminum nitride capacitors on silicon beams and measuring charge generation as each beam was deflected a known distance. These results provide parameters for films that enable accurate modeling and design of high frequency thin film bulk acoustic wave resonators.

TF-TuP21 Monochromatized Light Emitter using Si Doped Glass with Dielectric Multilayer Resonator*, **T. Ichinohe**,* Tokyo National College of Technology, Japan*; S. Nozaki, H. Morisaki,* The University of Electro-Communications, Japan*; S. Masaki,* Tokyo National College of Technology, Japan*; K. Kawasaki,* TDY Co. Ltd., Japan

Extensive studies have been made on nanometer sized Si ultrafine particle films (the Si nano-structured films) as a new functional thin film material applicable to Si based photo-electronic functional devices. Si-doped glass (Si-DG) films, especially, are expected because of the chemical stability and less aging degradation. However, they have wide bandwidth of luminescence spectral. To overcome the drawback for light emitter using Si-DG films, we fabricated a Fabry-Perot optical resonator with dielectric multilayer reflector. Both Si-DG films and multilayered reflectors were formed by the ion beam sputter-deposition (IBSD) technique. A conventional method to fabricate Si-DG films was the co-sputtering of a composite target, composed of Si chips placed on a SiO@sub 2@ target. The multilayer-reflecting mirror was fabricated by alternate sputtering of 5-inch CeO@sub 2@ target and Si/SiO@sub 2@ composite one. The quarter-wavelength optical thickness rule was used to design the multilayered reflector. To activate a Si-DG layer for a light emitter, the Si-DG film was heat-treated with about 900 °C. It was found that the heat-treatment was contributed to form Si nano particles with a diameter of about 3-4 nm estimated by TEM observation. The luminescent Si-DG film showed extremely broad PL spectra, the full width of half maximum (FWHM) being typically 1 eV. In order to improve the spectral distribution, the PL spectrum of Si-DG film with the optical cavity, which was sandwiched by metal (Ag) film and a dielectric multilayered reflector, reduced down about 0.1 eV, using a 20 paired CeO@sub 2@/Si-DG multilayer reflector. The application to EL device with the narrow band spectrum can be made by the improvement of contact electrode.

TF-TuP22 Measurement of Boron and Phosphorus Concentration in BPSG Thin Films Using FTIR and Artificial Neural Networks*, **M.F. Tabet**, W.A. McGahan,* Nanometrics Inc.

Borophosphosilicate glass (BPSG) thin films have been widely used in semiconductor device fabrication as interlayer dielectric films due to their excellent planarization, flow properties, and passivation barriers against moisture penetration. FTIR spectroscopy combined with chemometric techniques has been shown to accurately measure boron and phosphorus concentrations in BPSG thin films. A neural network is a set of simple, highly interconnected processing elements imitating the architecture of the human brain, which are capable of learning information presented to them. In this work Reflectometry measured at the same location as the FTIR is used to accurately measure film thickness. The thickness along with the FTIR data are then presented to a trained neural network which predicts the boron and phosphorus concentration in the film. Reflectance, FTIR and an independent measurement of concentration, XRF in this case, from a set of calibration wafers is required to train the neural network. Predicted concentrations from both calibration and test wafers were an average of 1 percent off XRF measurements. This measurement program was implemented on a Nanometrics NanoSpec 8000XSE, a standalone metrology tool, and will simultaneously measure thickness, index and both boron and phosphorus concentrations. This measurement can be easily transferred to the NanoSpec 9000, which is an integrated metrology tool. This measurement system is ultra-compact and was designed specifically for integration into semiconductor processing equipment. Integrated measurements of thickness, optical constants and dopent concentration would improve overall equipment effectiveness through advanced process control. This would provide process engineers immediate feedback and should reduce scrap and monitor wafers.

TF-TuP23 Investigation of the W-TiN Metal Gate for Metal-Oxide-Semiconductor Devices*, **S. Youn**, K. Roh, S. Yang, Y. Roh,* Sungkyunkwan University, Korea*; Y.C. Jang, K.S. Kim,* Sungkyunkwan University, Korea, South Korea*; N.-E. Lee,* Sungkyunkwan University, Korea

Several research groups recently proposed that W-TiN metal gate deposited on thin SiO2 may be suitable for the deep-submicron MOSFETs. Although the previous work demonstrates the promising results, the roles of TiN have not been systematically studied. We present experimental results in the present work that the change of Ar to N2 ratio during the TiN deposition by the reactive sputtering decides the crystallinity of LPCVD W, as well as the electrical properties of the W-TiN/SiO2/Si capacitor. In particular we show that the threshold voltage can be controlled via changing the Ar to N2 ratio. MOS capacitors were fabricated on 4~7@ohm@-cm, (100) p-type Si wafers. Thermal oxidation of the Si was carried out at 850°C for 80 s using RTP, resulting in an oxide thickness of ~110Å. TiN thin films were then deposited directly on SiO2 by a reactive sputtering system. The Ar/N2 flow was changed from 1/6 to 6/6 sccm. RTP was used for the annealing of TiN at 600-800°C for 3 min. Then LPCVD W films were deposited on TiN; the temperature, pressure, and flow rate were 350°C, 0.7 Torr, and WF6/SiH4/H2=5/10/500 sccm, respectively. The LPCVD W/SiO2/Si MOS capacitor was also fabricated to investigate the roles of TiN. As compared to the results obtained from the LPCVD W/SiO2/Si MOS capacitor, the insertion of approximately 20 nm TiN film effectively prohibits the fluorine diffusion during the deposition and annealing of W films, resulting in negligible leakage currents at the low electric fields. In addition, XRD analysis indicated that the preferred orientations of TiN and W films were determined by the change of Ar to N2 ratio. For example, if the ratio of Ar/N2 flow increases, a strong W(211) peak was developed and the resistivity of CVD W-TiN gate slightly decreases. In addition, the flatband voltage of MOS capacitors was shifted to the positive gate voltage when the ratio of Ar/N2 flow increases. We interpreted that this positive shift may be caused by the work-function difference that is caused by the incorporation of N2 during the sputtering process.

TF-TuP24 Effect of Interlayer on Thermal Stability of Nickel Silicide*, **J.S. Maa**, Y. Ono, F. Zhang, S.T. Hsu,* Sharp Laboratories of America, Inc.

Nickel silicide is one of the silicide material for future IC devices with ultra-shallow junctions. It has a low Si consumption rate. Low resistance nickel monosilicide can be applied easilly to sub-100nm structures. The major challenge is its poor therml stability for film of about 20nm. Here we study the effect of interlayer materials of Ti, Al, Pt, and Pd on the structure and thermal stability of nickel silicide. Ti and Al can enhance the epitaxial growth of nickel disilicide, but Pt can improve the thermal stability of nickel monosilicide. Pd was found not as effective as Pt. By using sequential deposition and RTA annealing, stable silicide can be formed on ultra-shallow junction with a 40nm junction depth. It is demonstrated that this structure is stable at 800 degree C with very low junction leakage.

TF-TuP25 Optical and Structural Properties of Sol-gel SiO@sub 2@ Layers Containing Cobalt*, A. Ramos-Mendoza, H. Tototzintle-Huitle, **A. Mendoza-Galván**,* CINVESTAV-IPN, México*; J. González-Hernández,* CINVESTAV-IPN, México, Mexico*; B.S. Chao,* Energy Conversion Devices, Inc.

SiO@sub 2@ layers containing cobalt in the range of 2 to 11 percent in volume were prepared using the sol-gel method. The layers with a thickness of about 600 nm were heat treated in air at 300 and 500 °C. Their structure and optical properties were characterized using optical transmission and reflection measurements, x-ray diffraction and Auger depth profile. The optical transmission data in the UV-visible range, of samples with low cobalt concentrations, show only the absorption bands corresponding to the tetragonal Co, regardless of the heat treatment temperature and the Co concentration. Layers with larger amount of Co, show absorption bands corresponding to both, tetragonal and octahedral Co. When these layers are heat treated, most of the cobalt migrates to the layer surface, being oxidized by the atmospheric oxygen, to form a conducting top layer of Co@sub 3@O@sub 4@, which thickness depends on the heat treatment temperature and Co concentratation. The presence of this top layer has been deduced from optical and Auger depth profile measurements. The cobalt oxide layer thickness ranges from about 100 to 7 nm. In order to describe the absorption bands of both, tetragonal and octahedral Co, it was used the Lorentz oscillator model for the complex effective dielectric function of the SiO@sub 2@ cobalt doped layers. The frequency dependence of the optical constants of the cobalt oxide top layer, in the UV-visible range, was obtained with a generalized Lorentz oscillator model. These latter results are in a good agreement with previous reports.

TF-TuP26 Perpendicular Magnetic Anisotropy in Ultrathin YIG Films Prepared by Pulsed Laser Deposition Technique*, **E. Popova,** N. Keller,* Versailles University, France*; F. Gendron,* Pierre and Marie Curie University, France*; M. Guyot, M.-C. Brianso, M. Tessier,* Versailles University, France

The development of high frequency and magneto-optical memory devices increases the interest in thin ferrite film preparation and investigation of their physical properties. A change of these properties is expected when the film thickness becomes of the order of a few lattice parameters. We report on thin and ultrathin yttrium iron garnet (YIG) film preparation by pulsed laser deposition technique. The films deposited on the quartz substrates are polycrystalline with slightly distorted lattice, though the average lattice parameter is the same as for bulk YIG (12.376 Å). The bulk Curie temperature of 557 K is observed for these films by means of magneto-optical Faraday rotation measurements. However, the saturation magnetization is slightly inferior to the bulk value in the range of 5 - 380 K. Ferromagnetic resonance (FMR) studies of samples with thickness 100 - 3800 Å were performed in different measurement geometries and in the temperature range of 3.5 - 300 K. We observed a change of sign of the effective magnetization (4@pi@M@sub eff@) appearing below a film thickness of approximately 120 Å. The inversion of the easy magnetization direction from in-plane to out-of-plane, i.e. the perpendicular magnetic anisotropy becomes evident above a cross-over temperature which is thickness-dependent. The effective magnetization for a given temperature decreased with decreasing sample thickness. This can be caused by an increasing contribution of the surface anisotropy to 4@pi@M@sub eff@ when the sample thickness is reduced.

TF-TuP27 Mechanical and Structural Characteristics of Nanocrystalline Diamond (NCD) and Diamond-like Carbon (DLC) Coatings*, **P. Jedrzejowski,*** Ecole Polytechnique de Montreal, Canada*; J. Grabarczyk, P. Niedzielski, S. Mitura,* Technical University of Lodz, Poland*; J.E. Klemberg-Sapieha, L. Martinu,* Ecole Polytechnique de Montreal, Canada

NCD and DLC films are increasingly attractive for the applications such as biocompatible coatings for metallic implants, anticorrosive protection or metallurgical coatings for tools. In the present work we fabricated NCD films by plasma enhanced chemical vapour deposition (PECVD) from methane using a novel high amplitude radiofrequency system. The film microstructure and mechanical properties were evaluated using Raman spectroscopy, elastic recoil detection, AFM, SEM, indentation and microscratch testing. We evaluated the effect of the structured intermediate carbide layer (interphase) on the film performance on substrates for medical applications such as AISI 316L steel, Vitalium and Titanium alloys. Breakdown voltage measured on samples exposed to Tyrod's solution was chosen as an appropriate technique to determine the coatings performance in simulated body environment. The NCD films are compared with standard DLC coatings.

TF-TuP28 Microstructure and Optoelectronic Properties of a-SiGe:H Thin Films Fabricated by the Low Frequency (55 kHz) Glow Discharge*, B.G. Budaguan, A.A. Sherchenkov, G.L. Gorbulin,* Moscow Institute of Electronic Technology, Russia*; A.A. Berdnikov,* Moscow Institute of Microelectronics of Russian Academy of Science, Russia*; V.D. Chernomordic,* Institute of Microelectronics of Russian Academy of Science*; **A.A. Aivazov,*** UniSil Corp.

The incorporation of Ge in a-Si:H allows to decrease the optical band gap which is necessary for a different optoelectronic applications such as infrared sensors, solar cells, etc. However the increase of Ge content leads to the increase of defects and to the deterioration of the electronic properties. So, the development of the appropriate fabrication technology of a-SiGe:H films is essential. We have shown that a-Si:H films with high electronic properties can be fabricated with using of low frequency (55 kHz) glow discharge. In this work we deposited a-SiGe:H for the first time by this method and investigated the growth mechanism, microstructure and optoelectronic properties of the layers. The a-SiGe:H films were fabricated at different germane content from 0 to 44.5%, and substrate temperatures, T@sub s@, from 175 to 275 °C. It was shown that the high deposition rate of a-SiGe:H is caused by an increased flux of radicals to the growth surface due to the close position of the radical generation region to the electrode. The joint analysis with using of infrared and atomic force microscopy showed that a-SiGe:H films have an island type morphology. The measurements of optoelectronic properties indicate that the decrease of the E@sub g@ with the increase of GeH@sub 4@ is determined by the increase of the concentration of Ge-Si bonds in the interior of islands, while the Si-H@sub n@ and Ge-H@sub n@ bonds are clustered on the island surfaces and does not affect the optical bandgap. The modeling of the photoconductivity showed that density of states distribution does not significantly change with the decrease of T@sub s@. Small decrease of photoconductivity accompanied by large decrease of dark conductivity leads to the high values of photosensitivity at lower temperatures for a-SiGe:H with E@sub g@ as low as 1.5 eV. Thus, 55 kHz glow discharge method allows to fabricate device quality low band gap a-SiGe:H films at low T@sub s@ and high deposition rate.

TF-TuP29 Deposition and Properties of Tetrahedral Carbon Films Prepared on Magnetic Hard Disks*, **C.Y. Chan,** K.H. Lai, M.K. Fung, I. Bello, R.F. Huang, C.S. Lee, S.T. Lee,* City University of Hong Kong, China*; S.P. Wong,* Chinese University of Hong Kong, China

The areal density of the hard disk doubles every two years. Such substantial increase in disk storage is due to the application of giant magneto-resistance (GMR) heads, new thin film media, and better electronic recording channels. However, such increment cannot be easily attained without reducing the separation between head and magnetic recording medium interface. This can be achieved by using thinner protective overcoating. Here, tetrahedral carbon (ta-C) ultra-thin films were deposited on magnetic hard disk (CoCrTa/Cr/NiP/Al-Mg) by magnetic filtered cathodic arc with variable substrate bias voltage. The resulting films exhibited smoother surfaces than those uncoated disks as indicated by atomic force microscopic measurements and gave rise to a single asymmetric Lorentzian Raman curve shape. Tetrahedral carbon coatings were subjected to an accelerated corrosion test in vapors of concentrated hydrochloric acid for 24 hours. The corrosion test showed the reduced density of corrosion sites when compared to conventional diamond-like carbon (DLC) films. Similarly, the scratch resistance of the ta-C coated disks, investigated by a nano-indenter, showed significant improvement in comparison to DLC films.

TF-TuP30 Properties of Multicomponent Transition Metal Carbide Coatings Prepared by Magnetron Sputtering*, **S.H. Koutzaki,** J.E. Krzanowski,* University of New Hampshire

The mechanical and tribological properties of conventional carbide hard coating materials can potentially be improved by developing multicomponent films with nano-scale microstructures. However, the microstructures and phases that form in PVD thin films are often far from equilibrium, so it is necessary to investigate these aspects of candidate multicomponent systems in order to assess their potential as nano-structured hard coatings. Two multicomponent metal carbide systems were investigated in this study, Ti-Mo-C and Ti-W-C. Coatings were fabricated by RF co-sputtering from carbide targets using target combinations of TiC-Mo2C and TiC-WC. Films were deposited on silicon and sapphire substrates at temperatures ranging from room temperature to 650C. The coatings were characterized by XPS, X-ray diffraction, TEM, and nanoindentation. For Ti-Mo-C films, nearly all film compositions were supersaturated solid solutions of Mo in TiC, and multiphase structures could only be obtained in highly Mo-rich films. The hardness of these films generally did not improve with Mo content. Films deposited from TiC and stoichiometric a-WC targets formed only (Ti,W)C solid solutions. The hardness of the sputtered Ti-W-C coatings was in the range of 15-17 GPa, with the exception of one Ti-W-C (40 %W) that had a hardness of 30 GPa. This latter sample was examined using high-resolution TEM, and in comparison to the other Ti-W-C films, was found to have a significantly smaller grain size and a higher film density.

TF-TuP31 Ferromagnetic Resonance and Magnetic Anisotropy in Epitaxial Fe/Ag Thin Films on GaAs (100)*, **W. Wu,*** University of California, Irvine*; C.S. Tsai,* University of California, Irvine and Academia Sinica, Taiwan*; C.C. Lee, H.J. Yoo, R. Chuang, H. Hopster,* University of California, Irvine

Iron/silver thin films were epitaxially grown on GaAs (100) substrate by molecule beam epitaxy (MBE) system at different growing temperatures and layer structures. Magneto-optic kerr effect (MOKE) experiment was used to measure the magnetization and sample magnetic anisotropy. The common features in the ferromagnetic resonance (FMR) peak-to-peak linewidth @delta@H@sub pp@ are identified, which are dependent on layer structures and growth condition. The measured narrowest linewidth @delta@H@sub pp@ is 26 Oe. We study the coupling between the ultrahigh frequency microwave signal and the spin excitation happened in ferromagnetic Fe thin film. Maximum coupling and thus strong attenuation of the microwave power occur at the FMR frequency f@sub res@ of Fe, as determined by the applied magnetic fields. Microwave notch filter devices were successfully fabricated using the deposited magnetic structures. Because of the high saturation magnetization of Fe film, it is much easy to achieve higher devices operation frequency under relatively lower applied magnetic field. The peak absorption carrier frequency of a propagating microwave has been tuned in a range from 9.6 to 21 GHz in a modest magnetic field from 0 to 2900 Oe for single layer structures. For multilayer structures, peak absorptions are intensified with tuned range from 10.6 to 27 GHz. The experimental results are in good agreement with the theoretical prediction for the case in which the magnetic field is applied along the easy axis of the Fe film. It is desirable to incorporate this kind of magneto static wave (MSW)-based devices in compound semiconductor system, in order to achieve integration into microwave integrated circuits.

TF-TuP32 Importance of Thermal Stress in a Thin Film Lipon Solid Electrolyte*, **F. Vereda**, R.B. Goldner, T. Haas,* Tufts University

Because a near term goal of our research is to obtain optimal performance physically vapor-deposited LiCoO@sub 2@/Lipon/C thin film batteries (Lipon = lithium phosphorus oxynitrade), and due to the major importance of the electrolyte in any battery, we have recently been attempting to better understand the causes of electronic shorting that affects our Lipon electrolyte films. After studying the residual and temperature-dependent stress of these films and observing severe cracking after they had undergone a relatively large thermal transient (from 300 °C to room temperature), we adopted a model in which a thermal expansion coefficient mismatch between Lipon and our glass substrates accounts for the cracking and therefore the shorting. This model was also supported by the fact that Al films, which proved to act as a 'buffer layer' and stopped cracking of Lipon when glass/Al/Lipon structures were cooled from 300 °C to room temperature, were successfully used to produce short-free Al/Lipon/Al devices.

TF-TuP33 Structural, Morphological, and Mechanical Properties of Plasma Deposited Hydrogenated Amorphous Carbon Thin Films: Noble Gas Dilution Effects*, **L. Valentini**, J.M. Kenny, G. Carlotti, G. Socino,* Universita di Perugia, Italy*; G. Mariotto, P. Tosi,* Universita di Trento, Italy*; L. Lozzi, S. Santucci,* Universita dell'Aquila, Italy

Recent studies of Ar dilution effects on hydrogenated amorphous carbon (a-C:H) films have been motivated by two factors: the possibility to synthesise diamond films at high temperature@footnote 1@ and the identification of the growth species. One way to pursue this issue consists in the investigation of the effects related to the dilution of methane by rare gases. In this paper a thorough investigation of a-C:H films deposited by rf glow discharge from methane-argon mixtures, for different Ar fractions, onto silicon substrate is presented. The structural, mechanical and morphological properties of these films were investigated by complementary techniques, such as x-ray reflectivity (XRR), Raman spectroscopy, Brillouin light scattering (BLS), tribology and atomic force microscopy (AFM). Experimental results are examined to develop a coherent picture of the relationships between deposition parameters, microstructural features and macroscopic properties, as well as to show how the results are found to be consistent with theoretical calculations@footnote 2@ that relates properties with different chemical composition of the plasmas. The effects due to film deposition parameters such as Ar dilution, applied substrate bias and film properties are discussed in order to clarify which process parameters are important in film formation. @FootnoteText@ @footnote 1@T.G. McCauley, D.M. Gruen, and A.R. Krauss, Appl. Phys. Lett. 73, 1646 (1998). @footnote 2@C. Riccardi, R. Barni, M. Fontanesi, and P. Tosi, to be published.

TF-TuP34 Structural Characterization of Tungsten Trioxide Thin Films*, **L.J. LeGore**, R.J. Lad, J.F. Vetelino, B.G. Frederick,* University of Maine*; E.A. Kenik,* Oak Ridge National Laboratory

Tungsten trioxide is a wide band-gap n-type semiconductor which has been used as a sensing material in conductance-type gas sensors. The microstructure and morphology is believed to have a large influence on the sensitivity, selectivity, and stability of the sensor. We have produced tungsten trioxide thin films 15 nm to 600 nm thick by reactive rf magnetron sputtering onto r-cut sapphire substrates. The microstructure of the films was characterized by reflection high energy electron diffraction (RHEED), transmission electron microscopy (TEM), and scanning electron microscopy (SEM). By controlling the substrate deposition temperature and by post-deposition annealing, films from highly oriented epitaxial to random polycrystalline were produced. All films were found to be dense with low porosity. The epitaxial films were nearly atomically smooth while the polycrystalline films were significantly rougher. Lattice parameter measurements at room temperature indicate the possibility of more than one crystallographic phase.

TF-TuP35 Study on the Oxidation Behavior of Poly Si @sub 1-x@Ge @sub x@ Films*, **S.-K. Kang**, D.-H. Ko,* Yonsei University, Korea*; S.-H. Oh, C.-G. Park,* Pohang University of Science and Technology, Korea*; T.-H. Ahn, M.-S. Joo,* Hyundai Electronics Industries Co. Ltd, Korea*; K.-C. Lee, D.-Y. Yang,* Ju-Sung Engineering Co. Ltd, Korea

We investigated the oxidation behavior of poly Si @sub 1-x@Ge @sub x@ films (X=0.15, 0.42). The samples were oxidized using a conventional furnace in wet oxygen ambient at 700 °C. The composition and thickness of oxide were analyzed by rutherford backscattering spectrometry (RBS) before and after the oxidation using rump simulation. The distribution and chemical bonding of Si, Ge, O elements were analyzed by X-ray photoelectron spectroscopy(XPS). The microstructures of the films were analyzed by HR transmission electron microscopy(TEM). In the case of poly Si @sub 0.85@Ge @sub 0.15@ films, SiO @sub 2@ was formed, rejecting Ge, and subsequently Ge content increased at the SiO @sub 2@/ poly Si @sub 1-x@Ge @sub x@ interface. We observed a small amount of Ge and GeO @sub 2@ in oxide layer by HR-TEM, XPS. In the case of poly Si @sub 0.58@Ge @sub 0.42@ films, we found the formation of both SiO @sub 2@ and GeO @sub 2@ on the poly Si @sub 1-x@Ge @sub x@ films due to the high Ge content. The oxidation rate of poly Si @sub 1-x@Ge @sub x@ increased with Ge content in poly Si @sub 1-x@Ge @sub x@ films under the same oxidation condition.

TF-TuP36 Mechanism of the Isothermic Amorphous-to-Crystalline Phase Transition in Ge:Sb:Te Ternary Alloys*, J. González-Hernández, E.F. Prokhorov, **Yu.V. Vorobiev**, E. Morales-Sánchez,* Centro de Investigacion y de Estudios Avanzados del IPN, Mexico*; A. Mendoza-Galván,* Centro de Investigacion y de Estudios Avanzados del IPN, Mexico, México*; S.A. Kostylev,* Energy Conversion Devices, Inc.*; Y.I. Gorobets, V.N. Zakharchenko, R.V. Zakharchenko,* Kiev Politechnic Institute, Ukraine

The kinetics of the isothermic amorphous-to-crystalline (fcc) phase transition at different temperatures has been investigated in alloys with the composition close to Ge@sub 2@Sb@sub 2@Te@sub 5@ which are the most frequently used for erasible optical memory devices. For monitoring the transformation, the electrical resistivity and capacitance measurements were employed as well as the ellipsometry, optical transmission and electron microscopy data. The procedure to determine the transformed volume fraction on the basis of the optical transmission and electrical conductivity data is analyzed. It is shown that the assumption widely accepted about the proportionality between the variation of transmittance or the conductivity and the transformed volume fraction, is seldom correct in the optical case, but never correct in the electrical one; the use of the corresponding procedure could give an error in determination of the crystalline volume fraction of about an order of magnitude. The correct procedure for this case is developed. The transformation kinetics observed agrees with the Johnson-Mehl-Avrami formalism, and gives an average Avrami exponent around 2 and the overall activation energy of about 4.5 eV; the latter value exceeds the previous estimations. The transformation process has the two well-defined stages corresponding to the bulk and surface nucleation of the crystalline phase, the sequence of the stages depends on temperature. It was also found that the ultimate degree of transformation in isothermic experiments is less than 1 and depends upon the transition temperature; the analytical description of this dependence is given. It is shown that this dependence influences the value of the phase transition activation energy determined from the experiment.

TF-TuP37 Dry Cleaning of Oxide and Contaminaions on Cu Surface in Water Ambient*, **H. Ogawa**, K. Taniguchi, Y. Horiike,* The University of Tokyo, Japan

A new cleaning method of the Cu bottom surface in via holes and gaps in the ULSI multi-level interconnection was studied employing in-situ XPS (ULVAC-PHI, model 1600). At first, reduction characteristics of the Cu native oxide (CuO and Cu@sub 2@O) on the Cu surface were investigated in N@sub 2@, H@sub 2@, O@sub 2@ and H@sub 2@O ambient at 1 Torr.

Analyses of Cu2p@sub 3/2@ photoelectron and Cu@sub LMM@ Auger electron spectra showed that CuO was reduced to Cu@sub 2@O in any ambient above 150 °C of sa mple temperature, because @DELTA@G@sub f@° of Cu@sub 2@O (-146 kJ/mol) is thermodynamically lower than that of CuO (-130 kJ/mol). Cu@sub 2@O was also found to be reduced to Cu in H@sub 2@, N@sub 2@ and H@sub 2@O ambient above 300 °C. H@sub 2@O dose not act as an oxidant for Cu, because @DELTA@G@sub f@° of H@sub 2@O (-229 kJ/mol) is lower than that of the Cu oxide. Next, oxide formation and hydrocarbon (CH@sub x@) and fluorocarbon (CF@sub x@) contaminations of the Cu surface were prepa red by exposure to ICP (inductively coupled plasma) of C@sub 4@F@sub 8@/Ar (unity partial pressure ratio, 20 mTorr of total pressure, 1 kW of 13.56 MHz, V@sub dc@=400V and 2 min) and subsequent O@sub 2@ (100 mTorr, 10 min) plasma. Then the surface was exp osed by the H@sub 2@O vapor ambient at 1 Torr. As a result, almost CH@sub x@ and CF@sub x@ contaminants were removed at 300 °C, and Cu oxides were completely reduced to Cu at 400 °C, while CH@sub x@ contamination was remained in N@sub 2@ and H@sub 2@ ambient at 400 °C. The reason of high removal efficiency of CH@sub x@ and CF@sub x@ in the H@sub 2@O ambient is considered that H@sub 2@O effectively acts as an oxidant and a reducing agent to these contaminations.

TF-TuP38 Characterization of the Reactive Species in an Atmospheric-Pressure Nitrogen Plasma*, G. Ding*, *S.E. Babayan, G. Nowling, R.F. Hicks,* University of California, Los Angeles

A nitrogen and helium plasma, operating at atmospheric pressure and powered by radio-frequency power at 13.56 MHz, has been investigated to understand the reaction chemistry for plasma-enhanced chemical vapor deposition of nitride materials. Spatial and temporal profiles of excited molecular nitrogen (A, B, and C states) were obtained by optical emission and absorption spectroscopy. In addition, the relative populations of the vibrational states of the ground-state nitrogen molecules were examined. The nitrogen atom concentration was attained by nitric oxide titration and by determining the rate constant for the recombination of nitrogen atoms to form the B state of excited molecular nitrogen. The concentration profiles of all these species were compared with a numerical model of the reacting flow. It has been found that the metastable molecular nitrogen and nitrogen atom concentrations are in the range of 10@super 12@ to 10@super 15@ cm@super -3@. Silicon nitride films were deposited on silicon substrates by combining silane with the effluent from the atmospheric pressure plasma source. Deposition rates of 100 nm/min were observed at substrate temperatures of 400±25 °C. After growth, the optical, electrical, and chemical properties of the films indicated that high quality silicon nitride was produced. The relationship between the film properties and the plasma chemistry will be discussed at the meeting.

Biomaterial Interfaces
Room 202 - Session BI+SS-WeM
Water at Biointerfaces

Moderator: B. Kasemo, Chalmers University of Technology, Sweden

8:20am **BI+SS-WeM1 Role of Water in Biological Processes***, E.A. Vogler,* The Pennsylvania State University **INVITED**

Water is so familiar and ubiquitous in our environment that we frequently forget, ignore, or underestimate the role its special properties play in the biological and material sciences. Likewise in the hybrid field of biomaterials, where water-surface interactions apparently control and/or moderate the biological response to materials applied in medicine and biotechnology. In fact, the behavior of water near surfaces is becoming increasingly relevant in these fields as surface-to-volume ratios increase with the ever-decreasing size imposed by micro-to-nano-scale analytical and medical devices, especially as applied in nanobiotechnology. This lecture reviews some important water properties from both a thermodynamic and molecular perspective. The occasionally forgotten biological/environmental importance of thermodynamic attributes such as heat capacity, (latent) heats of fusion/vaporization, density, and interfacial tension are briefly recapitulated, leading to the conclusion that terrestrial life simply could not and would not work the way it does without the special mediating influence of water. Molecular aspects that give rise to these important bulk-water properties will be discussed along with the impact these have on the mechanisms of water wetting. It will be suggested that current theories of wetting substantially ignore some of these unique aspects of molecular water that distinguish it from all other room-temperature fluids. Against this backdrop, evidence suggesting that the role of water in the acute biological response to materials has been underestimated will be presented, concluding that the interfacial behavior of water must be explicitly included in any comprehensive biophysical theory attempting to explain or predict performance of biology at aqueous interfaces.

9:00am **BI+SS-WeM3 Neutron Reflectivity Studies on the Interaction of Water with Biocompatible Monolayer Films***, D. Schwendel,* University of Heidelberg, Germany*; R. Steitz,* Hahn-Meitner Institute, Germany*; J. Pipper, R. Dahint, M. Grunze,* University of Heidelberg, Germany

Since the early 1990s protein resistance has been obtained for surfaces coated with poly- or oligo(ethylene glycol) (PEG or OEG) derivatives ((CH@sub2@-CH@sub2@-O)@subn@). While the inertness of PEG has been explained by the steric repulsion theory associating the inertness of the polymer brushes with the high conformational freedom of PEG chains in the near surface region, FT-IRRAS studies related the protein resistance of OEG to its molecular conformation. Whereas the helical and amorphous conformers on Au are inert towards protein adsorption, the planar all-trans conformer on Ag does adsorb protein. In Small Angle Neutron Scattering (SANS) studies we found experimental evidence for a strongly bound water layer on helical OEG-terminated alkanethiolate self assembling monolayers (SAMs). The experimental observations have been predicted by ab initio calculations simulating the adsorption of water molecules on methoxy terminated OEG with 3 EG units (EG3-OMe) and Monte Carlo simulations of water close to the SAM surfaces. Both theoretical studies postulate easy accommodation of water at helical OEG strands and a lower density of water near the SAM surface. This strongly bound water film is identified as the physical cause that these surfaces are inert against protein adsorption and cell attachment. SANS studies showed that the data for a hydroxy terminated helical OEG-SAM with 6 EG units (EG6-OH) on Au correlate satisfactorily with the model assuming a boundary water layer of 56 Å at the solid/liquid interface with a density of 92 % of that of bulk water. Also for the investigation of amorphous EG3-OMe immobilized on Au the assumption of a 36 Å water layer with a density of 78 % compared to bulk D@sub2@O yielded a much lower @chi@@super2@ deviation between the experimental data and the fit than the assumption of no interphase water.

9:20am **BI+SS-WeM4 Hydrogen Bond of Water in Ih Ice Probed by Core-level Spectroscopies***, **H. Ogasawara**, D. Nordlund, M. Cavalleri, L.-A. Näslund, M. Nagasono, L.G.M. Petterson, A. Nilsson,* Uppsala University, Sweden

In biological complexes, DNA, protein and so on, materials consist of two types of chemical bonds. A shorter covalent bond has the strength of a few eV to construct molecular flame, and longer hydrogen bond has the strength of a few tenth meV. This energetically weak nature of hydrogen bond gives flexibility and enables the self-organization of molecules at ambient temperature. Ice is a unique material that hydrogen and oxygen atoms in the crystal are connected both covalent and hydrogen bonds where each oxygen atom has two covalent O-H bonds and two hydrogen O-H bonds. Here we report electronic structure of water in Ih ice, a thin film grown on Pt(111), studied with combination of core-level spectroscopies, X-ray absorption spectrosocpy (XAS), X-ray emission spectroscopy (XES) and theoretical simulation (DFT calculation). The experiments were performed at MAX-LAB, Sweden. The details of the endstation is described elsewhere.@footnote 1@ The theoretical simulation of spectra was done using the deMon program@footnote 2@ XAS and XES results indicate a reconfigration of molecular orbitals of water in ice beside the binding energy shift. In O 1s XAS, 4a@sub 1@ resonance is severely suppressed indicating the enhancement of s-character of this orbital compared to that of the gas phase. In O 1s XES, 3a@sub 1@ emission is suppressed showing the strong s-character of this orbital. From these observations we conclude that a water molecule in ice has a pseudo-totally-symmetric character. This pseudo-totally-symmetric character of water in ice is confirmed by excitation profile of 3a@sub 1@ photoemission peak and theoretical simulation. @FootnoteText@ @footnote 1@ R. Denechke et al, J. Electron Spectrosc. Relat. Phenom. 101-103, 971(1999). @footnote 2@ deMon-KS version 4.0, deMon Software, (1997).

9:40am **BI+SS-WeM5 Tyrosine Derivatives Adsorbed on Gold for Surface Modification***, **K. Uvdal**, J. Svensson, P. Konradsson, B. Liedberg,* Linköping University, Sweden

Model molecules can be very useful when searching for mechanisms of protein folding. We intend to use model molecules to study if the changed conditions for binding of water, caused by binding and cleavage of ATP, is the main reason for protein conformational changes. In this very first study we are investigating tyrosine derivatives linked to 3-mercaptopropionic acid through an amide bond. Two different tyrosine derivatives, one with the OH group free and one with the OH group phosphorylated are studied. These molecules are adsorbed on gold and studied by X-ray Photoelectron Spectroscopy (XPS), Infrared Reflection-Absorption Spectroscopy (IRAS). The techniques are used to investigate the coordination to the surface and the molecular orientation of adsorbates relative to the surface. Molecular surface interactions causing chemical shifts in the core level XPS spectra of the adsorbates on gold are investigated using multilayer films as references. IR in transmission mode is used as a reference to the IRAS results and thus the surface selection rule is used to identify the orientation of certain vibrations relative to the surface. The S(2p) core level XPS spectrum for the adsorbate of the tyrosine derivative shows only one type of sulfur. The S(2p3/2) peak is shifted about 2.5 eV to lower binding energy when compared to multilayer showing a chemical adsorption through the sulfur atom. A phosphorylated tyrosine derivative adsorbed on gold shows an enhanced signal from PO3 in surface sensitive mode in good agreement with a molecular orientation with the PO3 group pointing away from the surface. The IR spectrum of the tyrosine derivative is showing several strong bands in transmission mode (KBr). Most of these peaks are also strong in the spectrum for the adsorbate. However, some significant differences are observed which are correlated to the molecular orientation relative to the surface. In a second step these monolayers are to be used for water interaction studies.

10:00am **BI+SS-WeM6 Stretching of a Macromolecule: A First Principles Theory***, **H.J. Kreuzer**,* Dalhousie University, Canada **INVITED**

The statistical mechanics to describe the stretching of a single polymer strand (in particular in an AFM experiment) is formulated. As ingredients one needs the potential energy surfaces of the various conformers of the macromolecule. These have been calculated for oligo (ethylene glycol) resulting in quantitative agreement for the force/extension curves measured for PEG, both in hexadecane and in water. The interaction of water with PEG is discussed in great detail. We also present results for the effect of strong electric fields on PEG, such as surprisingly large electrostriction.

10:40am **BI+SS-WeM8 A Fundamental Approach to Protein Adsorption: Changes in Free Energy for Adsorption of Individual Peptidyl Residues onto Functionalized SAM Surfaces***, **R.A. Latour**,* Clemson University*; L.L. Hench,* Imperial College, UK

Cellular response to biomaterial surfaces has great importance for the design of bioactive substrates for implant, drug delivery, and tissue engineering applications and is greatly influenced by protein/surface adsorption. All proteins are made up of amino acids (peptidyl residues); thus protein adsorption must be fundamentally governed by the submolecular interactions between a protein's residues and surface functional groups. The objective of this research was to develop an approach to quantitatively determine changes in Gibbs free energy for individual mid-chain residue/surface (R/S) functional group interactions and apply it to selected R/S group pairs. Molecular models (MOPAC/COSMO; CAChe software, Oxford Molecular Inc.) were created of 3 residues (Ala, Ser, Lys) and 3 SAM surfaces (CH@sub 3@, OH, COO-) to represent hydrophobic, hydrophilic, and charged systems in an aqueous environment. Adsorption enthalpy for each R/S pair was determined by positioning the residues over the surfaces and calculating the system energy as they were sequentially separated from the surface. Additional enthalpy and entropy contributions due to water restructuring effects were estimated based on changes in solvent accessible surface area and experimental wetting data. This was combined with the modeling data to calculate the net @DELTA@G@sub ads@. Ala was predicted to tightly bind to the CH@sub 3@ surface with @DELTA@G@sub ads@ = -5.8 kcal/mol with Ser and Lys each having @DELTA@G@sub ads@ > 0. All 3 residues exhibited @DELTA@G@sub ads@ > 0 for adsorption to the OH surface. Lys was predicted to be attracted to the COO- surface with @DELTA@G@sub ads@ = -5.4 kcal/mol, but only through intervening water layers with a 5 - 7 Å surface separation distance. Ala and Ser had @DELTA@G@sub ads@ > 0 for their interaction with the COO- surface. Further work is planned to integrate this type of data to develop a universal model for predicting protein-surface adsorption behavior.

Dielectrics
Room 312 - Session DI+EL+MS-WeM
Low K Dielectrics

Moderator: J.A. Kelber, University of North Texas

8:20am **DI+EL+MS-WeM1 Ultra Low k Mesoporous Silica Dielectrics for Semiconductor Interconnects**, ***S. Baskaran***, *J. Liu, X. Li, C. Coyle, J. Birnbaum, G.C. Dunham, G.E. Fryxell,* Pacific Northwest National Laboratory; *C. Jin,* International SEMATECH **INVITED**

The semiconductor industry is currently targeting new intermetal dielectric (IMD) films with dielectric constants (k) less than 2.5 for interconnect applications in the 100 nm technology node, and films with k less than 2.0 for the 70 nm technology node. To meet extreme low k needs for advanced on-chip interconnects, films with incorporated porosity will most certainly be required. Porous dielectric films with k values less than 2.2 ("ultra low k") are not easily synthesized using conventional vacuum based technology such as chemical vapor deposition. A simple approach to nanoporous dielectric films involves spin-on deposition of formulations consisting of silicate, polymeric, or hybrid organosilicate precursors with thermally degradable pore-formers. Ultra low k mesoporous silica films have been synthesized with molecularly templated porosity using this approach. Molecularly organized nanostructured aggregates between 2 and 10 nm in size can function as templates for pore formation in spin coated sol-gel silicate films. The use of a structurally organized template during synthesis results in a uni-modal pore size distribution in the final film. In this paper, we present information on precursor chemistry for designing mesoscale porosity, pore architecture and surface chemistry, and the critical dielectric and mechanical properties for mesoporous silica films. Using formulations developed at PNNL, mesoporous films have also been prepared at SEMATECH on production-size wafers, and evaluated. Copper single-damascene one-level test structures were built using mesoporous silica as the intermetal dielectric. No major structural failures were observed after chemical mechanical planarization on both blanket films and patterned wafers, indicating relatively good mechanical integrity for a highly porous structure. With controlled film synthesis and dehydroxylation conditions, mesoporous silica films with k@super 2@ 2.0 and elastic modulus of 4.0 GPa have been synthesized at PNNL. The results of the one-level metal screening tests at SEMATECH combined with properties obtained at PNNL indicate that mesoporous molecularly-templated silicate films hold promise as ultra low k intermetal dielectrics.

9:00am **DI+EL+MS-WeM3 Deposition of Thermal Stable Amorphous Carbon Nitride Thin Films with Low Dielectric Constant by ECR-CVD**, *X.W. Liu,* National Tsing Hua University, Taiwan, ROC, Taiwan,ROC; *J.H. Lin,* National Tsing Hua University, Taiwan, ROC; ***H.C. Shih,*** National Tsing Hua University, Taiwan, ROC, Taiwan,ROC

Amorphous carbon nitride thin films with low dielectric constants and high thermal stability were synthesized on silicon by using an electron cyclotron resonance chemical vapor deposition (ECR-CVD) system in which a rf bias was applied to the silicon substrate and a mixture of C@sub 2@H@sub 2@, N@sub 2@ and Ar was used as precursors. The dielectric constants of our amorphous carbon nitride thin films were found as low as 2.4 at 1 MHz. The thermal stability of the films has been improved by the incorporation of nitrogen to the carbon film. The basic structure, composition and electronic properties of these films were analyzed by Fourier transformation infrared (FTIR) spectroscopy, Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM), and field emission scanning electron microscopy (FE-SEM) and dielectric constant measurements.

9:20am **DI+EL+MS-WeM4 Impact of Hydrogen Addition on the Deposition Rate of SiOF Films Prepared by High Density Plasma CVD**, *Y.W. Teh,* Nanyang Technological University, Singapore; *T.C. Ang,* Chartered Semiconductor Manufacturing, Singapore; ***K.S. Wong***, Nanyang Technological University, Singapore; *K.H. See, S.Y. Loong, Y.C. Wong,* Chartered Semiconductor Manufacturing, Singapore

Fluorinated Silicon Dioxide film (SiOF) has been considered as the more successful first generation interlevel low-k dielectric material. However, the impact of hydrogen addition on SiOF film properties are not extensively studied. In this paper, we present a spectroscopic study of the chemical bonding in SiOF film grown with silane gas added to the standard precursors using the techniques of ellipsometry and infrared (IR) absorption spectroscopy. These SiOF films have been prepared by high density plasma (HDP) chemical vapor deposition at substrate temperature at about 420°C. Addition of hydrogen through silane gas feed is found to control deposition rate and the fluorine doping concentration of the SiOF films. The addition of SiH4 does not lead to the incorporation of hydrogen in detectable quantities in the SiOF films. This phenomenon may be attributed to the strong mutual attraction between hydrogen and fluorine radicals in the HDP. The decrease of refraction index at 632.8nm and the frequency decrease of the dominant IR active bond-stretching vibration at ~1085cm@super -@@super 1@ were found to be approximately linear with increase in fluorine concentrations. The silane added to the process gas mixture has been found to play an active role in the SiOF film formation process both in the surface reactions and the chemical bonding properties. Our results show that with an optimized silane flow rate, the film stability of the SiOF towards moisture attack is significantly improved. In addition, a high deposition rate can be achieved together with comparable fluorine incorporation in the film as compared to the standard non-silane precursors.

9:40am **DI+EL+MS-WeM5 Solid-state Nuclear Magnetic Resonance of Low Dielectric Constant Si:O:C:H Films**, ***P.-Y. Mabboux***, *K.K. Gleason,* Massachusetts Institute of Technology

Adding organic content to SiO@sub 2@ is an evolutionary pathway to low dielectric films with k @<=@ 3.0. Alternate names for these materials include carbon-doped oxides, organosilicate glasses (OSG), and Si:O:C:H films. Both spin-coating and chemical vapor deposition (CVD) processes have been developed for this class of low-k films. Fourier transform infrared spectroscopy (FTIR) and x-ray photoelectron spectroscopy (XPS) have only a limited ability to distinguish variations in Si:O:C:H film chemistry. In this work, solid-state nuclear magnetic resonance (NMR) is shown to have sufficient sensitivity to determine the network structure of low dielectric constant Si:O:C:H films. Characterization of Si:O:C:H films by @super 1@H, @super 13@C, and @super 29@Si magic-angle spinning NMR will be demonstrated. Because of its wide range of chemical shifts, @super 29@Si NMR is particularly useful to elucidate new details regarding the composition and structure of these low dielectric constant films. Up to ten different environments can be resolved in some of the films. Many of the observed chemical bonding configurations have been previously observed in bulk organosilicate glasses. The NMR results can be expressed in terms of a connectivity number, which is simply the average number of bonds between network forming atoms. The connectivity number may provide a means to correlate with the mechanical properties. Fundamental understanding of structure-property-processing relationships will facilitate the engineering of the molecular architecture required for successful integration of Si:O:C:H dielectric films.

10:00am **DI+EL+MS-WeM6 A New Simple and Accurate Method to Measure Intra-Metal Capacitance of Low-K Fluorinated Silicon Dioxide**, *K.S. Wong,* ***Y.W. Teh***, Nanyang Technological University, Singapore; *T.C. Ang, S.Y. Loong, W.B. Loh, Y.C. Wong,* Chartered Semiconductor Manufacturing, Singapore

An accurate and simple technique for intra-metal capacitance measurement is presented. This on-chip technique is based on a test structure design that utilizes only interdigitated capacitors sandwiched between metal plates. Compared to other techniques which utilize transistors in addition to the unknown interconnect capacitance to be characterized, this new technique requires only capacitors and thus much simpler processing and shorter cycle times but with the same level of accuracy. With this test structure design, no reference capacitor is needed. Capacitance voltage (C-V) method is commonly used for intra-metal capacitance measurement. However, the measurement accuracy is often compromised by probe-induced stray capacitance. In this paper, a new measurement technique that can eliminate this stray capacitance is reported. This new technique uses multiple probe configurations to obtain 3 capacitance values and these values can be used to eliminate the probe-induced stray capacitance and obtain the actual intra-metal capacitance. Results show much better accuracy than the conventional C-V measurement. Comparisons between the new technique, the conventional C-V measurement and the Charge-Base Capacitance Measurement (CBCM) techniques are made. Our results based on the new technique show great improvement in the measurement accuracy over the conventional technique. In addition, our results are consistent with the results obtained from the CBCM technique which requires the use of transistors and thus more complex processing and longer cycle times. In this paper, the different measurement techniques were evaluated on high-density plasma chemical vapor deposition (HDP-CVD) fluorinated silicon dioxide (SiOF) inter-level dielectric (IMD) films in 0.18um technology.

10:20am **DI+EL+MS-WeM7 DC and RF Characteristics of Advanced MIM Capacitors for MMIC's Using Thin and Low Temperature PECVD Si@sub 3@N@sub 4@ Dielectric Layers***, **C.R. LIM**, J.H. LEE, S.W. Paek, K.W. Chung,* LG-ELITE, Republic of Korea

In this work, we show the excellent DC and RF characteristics of MIM (metal-insulator-metal) of PECVD Si@sub 3@N@sub 4@ thin film deposited at 85°C. The breakdown field strength of MIM capacitors with 490 Å Si@sub 3@N@sub 4@ was larger than 4.1 MV/cm which indicates the excellent quality of the deposited Si@sub 3@N@sub 4@ film. The main capacitance of unit area extracted by RF (radio frequency) measurements was 1240 pF/mm@super2@. So, its high capacitance enables us to reduce the size of MIM to a quarter size compared with the conventional MIM having 2000 Å Si@sub 3@N@sub 4@. In spite of its thin thickness of dielectrics, RF characteristics showed good performance. Above all, it was fabricated at low temperature, so we were able to develop the process of MIM fabrication using dielectric lift-off. At this point, the thickness adapted in dielectric lift-off process was about 1000 Å for adjusting capacitance to a designed capacitance.

10:40am **DI+EL+MS-WeM8 Rapid Prototyping by Local Deposition of Siliconoxide and Tungsten Nanostructures for Interconnect Rewiring***, H.D. Wanzenboeck, S. Harasek, H. Langfischer, A. Lugstein, **E. Bertagnolli**,* Vienna University of Technology, Austria

The local deposition of dielectric material and metal wires as typically used for rewiring of interconnect layers has been demonstrated to be a promising approach for rapid prototyping of integrated circuits. With an ion beam induced surface reaction dielectric structures were fabricated with a selected geometric configuration in dimensions ranging from several hundred Âµm down to the deep sub-Âµm scale displaying the potential application in interconnect modification. A focused Ga ion beam at 50 kV acceleration voltage was applied to induce the surface decomposition of gaseous precursors. A dynamic adsorption state was achieved characterized by the equilibrium between influx through a nozzle system and the outlet through the vacuum pump. Siliconoxide was obtained by using siliconorganic compounds and oxygen as precursor adsorbed on the surface at a total pressure typically between 10E-5 to 10E-6 Torr. Conductive W-structures were obtained using W(CO)6. The suitability for practical applications in microelectronics has been demonstrated by measuring the electrical properties of deposited dielectrics using test vehicles with a metal-insulator-metal (MIM) capacitor setup. The thickness of the dielectric layer was varied between 70 nm and 1.4 Âµm. The resistivity and capacitance of FIB deposited dielectrics was found to vary with deposition parameters such as exposure time and scanning rate of the ion beam. A chemical characterization of the fabricated dielectric layers has been performed. The electrical properties of locally deposited dielectrics were correlated with the material composition of the deposited material. The suggested optimized deposition process can provide improved dielectrics suitable as interline and interlayer insulator for a complex microelectronic interconnect architecture.

Incorporating Principles of Industrial Ecology
Room 304 - Session IE+PS+MS+SE-WeM

Environmentally Friendly Process Development

Moderator: D.R. Baer, Pacific Northwest National Laboratory

8:20am **IE+PS+MS+SE-WeM1 CVD Films as Directly Patternable Low-k Dielectrics***, **K.K. Gleason**, H.G. Pryce Lewis,* Massachusetts Institute of Technology*; G.L. Weibel, C.K. Ober,* Cornell University **INVITED**

As microelectronic feature sizes decrease to 100-nm and below, major advances in both interconnect and lithographic technologies are necessary. Novel low-k candidates being assessed include fluorine- and silicon-containing materials produced by chemical vapor deposition (CVD). Fluorine- and silicon-containing polymeric materials are also ideal resist candidates for 157-nm photolithography, as conventional photoresists are opaque at this wavelength. In this paper, we present a collaboration aimed at merging the role of sacrificial resist and low-k dielectric. Specifically, we are investigating a direct dielectric patterning process in which a low-k fluorocarbon or organosilicon material is deposited by CVD, exposed, and developed using no wet processing. In our scheme, a film is deposited using hot-filament CVD, a non-plasma technique which offers the ability to tailor film chemistries. The film is masked and exposed using e-beam or a 157-nm source, and developed using supercritical CO@sub 2@ as a dry developing medium. The patterned film then serves as a low-k material compatible with metallization schemes such as the damascene process. This technology would greatly simplify future device manufacture by reducing the number of steps involved in patterning. The CVD process and the use of dry development also offer environmental, safety and health advantages over solvent-based spin-on coating and aqueous development. Positive-tone contrast has been demonstrated in fluorocarbon CVD films and fully-developed images of 0.25-micron have been demonstrated from e-beam exposure. We are presently working to enhance sensitivity and optimize image resolution.

9:00am **IE+PS+MS+SE-WeM3 Characterization of Remote Plasma Clean Process for Plasma CVD Chamber***, **T. Tanaka**, T. Nowak, M. Seamons, B.H. Kim, K. Lai, M. Cox, P. Loewenhardt, D. Silvetti, S. Shamouilian,* Applied Materials Inc.

Remote plasma cleaning of CVD process chambers has proven to be more efficient than conventional in-situ plasma cleaning in terms of higher throughput and higher gas breakdown efficiency. It is still important, however, to maximize the efficiency of the remote plasma clean process because of the potential environmental impact and the cost of process gases. The remote clean process involves three steps: generation of reactive species (mostly fluorine atoms) in a remote plasma source, transport of the reactive gas, and the cleaning reaction in the CVD chamber. We studied the efficiency of the process in each step. Since accurate direct measurement of the atomic fluorine concentration in the various parts of the CVD reactor is difficult, we used etching of thermal oxide wafer coupons to estimate the relative distribution of atomic fluorine within the reactor. Source dissociation efficiency was studied using an indirect technique based on correlation of pressure to effluent composition. We found that it requires approximately 24eV to break down each NF@sub 3@ molecule. This translates to 1.7W/sccm of NF@sub 3@ flow. This was seen to be approximately the same for both a microwave discharge operating at 2.45GHz and an inductively coupled plasma at 13.56MHz. Results characterizing the transport step demonstrate the importance of system design on minimizing recombination losses of the reactive species which, for a parallel plate reactor, can be as high as 50% of the atomic fluorine generated in the remote plasma source. The experimental results are compared with a simple model, which describes the general behavior of the cleaning process.

9:20am **IE+PS+MS+SE-WeM4 Silicon Oxide Contact Hole Etching Process Employing Environmentally Harmonized Technique***, **K. Fujita**, M. Hori, T. Goto,* Nagoya University, Japan*; M. Ito,* Wakayama University, Japan

Etching process of SiO@sub 2@ contact holes in ULSI has been developed by using high-density plasmas employing stable PFC gases. PFC gases, however, cause a serious environmental problem, namely global warming and hereby the uses of fluorocarbon gases would be restricted in the near future. Recently, we proposed environmentally harmonized technique replacing stable PFC gases for preventing global warming, where polytetrafluoroethylene (PTFE) is evaporated by a CO@sub 2@ laser and the generated fluorocarbon species (C@sub x@F@sub y@) are injected into ECR plasma reactor from externally. This technique, therefore, enables us to achieve a novel plasma process with new gas chemistries. In this study, this system has been successfully applied to ECR plasma etching of SiO@sub 2@ contact hole and the behavior of CF@sub x@ (x=1-3) radical densities in the plasma were evaluated by infrared diode laser absorption spectroscopy (IRLAS). The high SiO@sub 2@ etching rate of 780 nm/min was obtained at a microwave power of 400 W, a pressure of 2.7 Pa, a total flow rate of 80 sccm and a bias voltage of -450 V. Dependence of contact hole etching characteristics on Ar dilution and pressure has been investigated. Anisotropy of contact hole etching was improved with increasing the Ar dilution ratio and decreasing the pressure because the fluorocarbon polymer deposition was suppressed at the higher Ar dilution and the lower pressure. IRLAS measurements indicate CF@sub 2@ radicals and higher radicals (C@sub x@F@sub y@) have the good relation with the polymer deposition. The anisotropic contact hole etching was achieved at an Ar dilution ratio of 90 %, a pressure of 0.4 Pa and the etching rate of SiO@sub 2@, selectivity of SiO@sub 2@ to Si and selectivity of SiO@sub 2@ to resist were 340 nm/min, 31 and 6.4, respectively. These results indicate that this environmentally harmonized technique will propose the alternative etching system replacing PFC gases.

9:40am **IE+PS+MS+SE-WeM5 Photocatalytic, Anti-fogging Mirror***, **K. Takagi**,* ULVAC Japan, Ltd., Japan*; H. Hiraiwa, T. Makimoto, T. Negishi,* ULVAC Japan, Ltd.

Recently, environmental pollution is growing more serious everyday, and it is urgently required to develop resource-saving and non-chemical products, which may save and even purify the nature. In such circumstances, titanium dioxide (TiO@sub 2@) thin coating film has come into the spotlight as a savior of the environmental problems. Because of its attractive photocatalytic natures, such as anti-bacterial, self-cleaning, decomposition of organic substances, and super-hydrophilic natures, TiO@sub 2@ has been studied and developed energetically in these days. Already, its super-hydrophilic and self-cleaning natures are applied to automobiles' anti-fogging side mirrors, which are now in practical use, and ULVAC Japan is one of the top makers for manufacturing vacuum deposition system for anti-fogging mirrors. The film architecture of this mirror is the double layer of SiO@sub 2@ / TiO@sub 2@ on the substrate coated by E/B evaporation or sputtering. The photocatalytic natures are as follows; 1. The contact angle of water on this surface is less than 10@Ao@ after irradiation of Blacklight, on which the engine oil is spreaded and cleaned by washing. 2. The contact angle keeps less than 10@Ao@ when this sample is preserved in the dark room. This report describes current developmental status of vacuum deposition system for TiO@sub 2@/SiO@sub 2@ thin film coating that is applied to automobile-mounted photocatalytic mirrors and is useful for environment saving and purification.

10:00am **IE+PS+MS+SE-WeM6 Low-k Materials Etching in Magnetic Neutral Loop Discharge Plasma***, Y. Morikawa, S. Yasunami,* ULVAC JAPAN Ltd.*; W. Chen, **T. Hayashi**,* ULVAC JAPAN Ltd., Japan*; H. Yamakawa, T. Uchida,* ULVAC JAPAN Ltd.

Many low-k materials, like Si containing inorganic / organic compounds, purely organic compounds and porous silicate glass, are proposed and examined as the interlayer dielectric one. The magnetic neutral loop discharge (NLD) plasma is very useful for very fine pattern etching process, because the NLD plasma has high density and low temperature characteristics and tends to form uniform density distribution on the substrate, at lower pressure region than 1 Pa under 13.56 MHz oscillating induction field.@footnote 1-3@ So we adopted the NLD plasma to etch organic low-k materials, with very high etch rate over 900 nm/min by using NH@sub 3@. An etching issue for the purely organic low-k materials is bowing in the hole smaller than 200nm in diameter, probably caused by reaction of the hole-wall surface with hydrogen atoms. Based on this consideration, we carried out the etching by using nitrogen gas mixed with a low concentration of hydrogen gas in low pressures below 1 Pa. The etch rate increased abruptly at hydrogen addition of a few quantity and approached gradually to a constant value at 20%. But the bowing size became larger above hydrogen mixed ratio of 20%. So we measured mass spectra of ion species produced in the plasma to know the mechanism. It was found that intensity of N2H+ also increased abruptly and then was close to a constant value at 20%. The other species did not show similar tendency. It is deduced from this result that N2H+ ion may participate in main etching reaction to obtain the conformal etched profile. Etching characteristics for OSG, pure organic low-k materials and porous silicate glass will be shown. @FootnoteText@@footnote 1@W.Chen, T.Hayashi, M.Itoh, Y.Morikawa, K.Sugita, H.Shindo and T.Uchida : Jpn. J. Appl. Phys., 38 (1999) 4296 @footnote 2@W.Chen, T.Hayashi, M.Itoh, Y.Morikawa, K.Sugita and T.Uchida : Vacuum, 53 (1999) 29 @footnote 3@W.Chen, T.Hayashi, M.Itoh, Y.Morikawa, K.Sugita, H.Shindo and T.Uchida : J. Vac. Sci. Technol. A17(5), (1999) 2546.

Material Characterization
Room 207 - Session MC-WeM

Methods of Data Analysis

Moderator: D.G. Castner, University of Washington

8:20am **MC-WeM1 Interpretation of the Shirley Background in XPS Analysis***, **J.E. Castle**,* University of Surrey, U.K. **INVITED**

The feature that is perhaps the most characteristic of an XPS spectrum, i.e. the step in background which accompanies every peak, is also its most enigmatic. The simple interpretation given in early texts was that the step is created by extrinsic losses as the electron travels through the material has not survived the work of Tougaard@footnote 1@ who has shown that the extrinsic losses build up rather slowly on the low kinetic energy side of the peak. In fact when the Tougaard function is subtracted from a typical peak there remains a peak with a considerable tail. Interpretation of this tail in a quantitative manner has always posed problems, mainly because the standards used for sensitivity factors do not include the tail and in most cases of analysis the tail extends beyond the window used for the narrow scan. Thus to undertake quantification in XPS analysis it is normal to remove a background which is based on the original Shirley algorithm,@footnote 2@ i.e. an integration of the peak lying above background using an integration constant which allows the background to merge with the experimental data at some point close to the peak. A browse through a collection of standard xp spectra of the elements quickly reveals what many of us recognise from experience: That the intensity removed by the Shirley background differs from one element to another. Over the past few years, working with Pr.A.M.Salvi, we have shown that this part of the background structure varies in a systematic manner across a row of the periodic table. In this review we bring together results published in several journals@footnote 2-6@ in an attempt to give a unified account of the progress so far made. It will be shown that the intensity of the background can be distinguished from the Tougaard, extrinsic loss, background and characterised by a single parameter. This 'shape' parameter can be of value in peak fitting, especially when fitting over lapping peaks as occurs with oxide films on metals. There is also an element of chemical state information contained in the peak itself. For example we have shown that when aluminium participates in the formation of an aluminide with one of the 3d transition metals, then the aluminium gains the background imprint typical of the 3d elements. Similar findings occur in the formation of other covalent compounds and in the chemisorption of molecules to transition metal substrates. In conclusion the review will show that the Shirley background, far from being part of the spectrum to be discarded, actually contains information of a secondary nature which can be useful in interpretation of the primary analytical results. @FootnoteText@@footnote 1@S. Tougaard, Applied Surface Science, 100/101, pp 1-10 (1996) @footnote 2@D.A. Shirley, Phys.Rev.B, 5 4709 (1972) @footnote 3@Anna Maria Salvi and James E Castle, J. Elec Spec & Related Phenomena, 94 pp 73-88 (1998) @footnote 4@Anna Maria Salvi and James E Castle, "The intrinsic asymmetry of Photoelectron Peaks: Dependence on Chemical State and Role in Curve Fitting", J. Elec Spec & Related Phenomena, 95 pp 45-56 (1998) @footnote 5@J.E.Castle, S.J.Greaves, M.R. Guascito, and A.M.Salvi, "A New Probe of Bonding States in Intermetallic Compounds" Phil Mag. 79, pp 1109-1129 (1999). @footnote 6@J.E.Castle, A.M.Salvi*, M.R. Guascito, "A Substrate-Related Feature in the Loss Structure of Contamination-C1s" Surface and Interface Analysis, 27, 753 - 760 (1999) @footnote 7@J.E.Castle, H.Chapman-Kpodo, A.Proctor** and A.M.Salvi*"Curve-Fitting in XPS Using Extrinsic and Intrinsic Background Structure" J.Elec.Spec.and Rel Phenomena, 106 pp 65-80 (1999)

9:00am **MC-WeM3 Formation of Potentially Protective Oxide-free Phosphate Films On Titanium Characterized by Valence Band X-ray Photoelectron Spectroscopy***, J.A. Rotole,* Kansas State University*; K. Gaskell,* Nottingham Trent University, UK*; A. Comte,* Ecole Nationale Superieure de Chimie de Clemont-Ferrand, France*; **P.M.A. Sherwood**,* Kansas State University

This paper reports the results of a continuing study focused on preparing novel surface chemistries on metal surfaces. In this paper we report how it is possible to prepare oxide-free titanium metal surfaces protected by a film consisting of phosphate. The surface is prepared by electrochemical treatment in an anaerobic cell which allows electrochemistry to be conducted on samples located in a vacuum system attached to an X-ray photoelectron spectrometer. When a clean metal surface is subjected to electrochemical treatment in aqueous orthophosphoric acid an oxide-free phosphate film can be formed on the metal which is stable on subsequent air exposure. Compositional variations were found with potential and other factors. Identical electrochemical treatment of as received titanium foil in atmosphere yielded samples that had a surface consisting largely of oxide. The chemical composition of these surface films was studied by core level and valence band X-ray photoelectron spectroscopy. Valence band photoemission interpreted by band structure calculations was found to be especially effective in understanding subtle differences in surface chemistry, enabling the clear identification of phosphate (being able to distinguish between orthophosphate and metaphosphate films) and its distinction from surface oxide.@footnote 1@ @FootnoteText@ @footnote 1@ This work was funded by the National Science Foundation under grant CHE-9421068.

9:20am **MC-WeM4 Chemometric Approaches to the Analysis of Surface Chemical Image Data**, ***K.G. Lloyd,*** *D.J. Walls, G.S. Blackman, N. Tassi, J.P. Wyre,* E.I. DuPont de Nemours and Co., Inc. **INVITED**

ToF-SIMS (Time-of-Flight Secondary Ion Mass Spectrometry) provides a mass spectrum from the topmost 10-20 Angstroms of a sample, which is in effect a composite of mass spectra from all species that co-exist at the surface. This makes it difficult to track surface compositional changes in multi-component systems, especially when molecular ions are not observed. In the area of chemical imaging, the generally comparable secondary ion yields from most organic species result in little/no contrast observed in total ion images of organic/polymeric samples. Recent advances in technology now allow us to acquire an entire spectrum at each image pixel. This approach results in a huge amount of data and requires an objective, robust, and automated means of data analysis. For all these reasons, chemometric methods such as Principal Components Analysis (PCA) and Partial Least Squares (PLS) have come to play an important role in surface characterization, not just for ToF-SIMS, but for all the surface chemical imaging techniques. We have had considerable success with the use of chemometric approaches for visualizing chemical contrast in chemical images from ToF-SIMS, Raman, and ESCA data. Our work has focused on how to take advantage of the complementary information content of these data sets. This talk will present examples of how we are using these multivariate statistical techniques today, and how we might expect to use them in the future.

10:00am **MC-WeM6 Multivariate Analysis of TOF-SIMS Data of Dodecanethiol SAMs: Detailed Spectral Analysis and Insight Into Fragmentation**, ***D.J. Graham,*** *B.D. Ratner,* University of Washington

The analysis of novel engineered surfaces will require detailed, molecular specific characterization methods. The power of multivariate analysis in extracting such detailed information from TOF-SIMS spectra of a time series assembly of dodecanethiol SAMs was studied. PCA analysis of the negative spectra showed a relative increase in the intensity of molecular ion clusters and low mass hydrocarbon fragments (C to C3) with increasing time. This trend was also reflected in the positive data where a relative increase of C to C4 hydrocarbon fragments was seen at longer assembly times. This increase was accompanied by a relative decrease in the intensity of C5 and above hydrocarbon fragments. To assure these trends were not just an artifact of the PCA analysis we plotted the original spectral data from the peaks involved in the above trends. These plots verified that the trends seen in the PCA analysis reflected actual trends in the TOF-SIMS data. This data suggests that as the SAM surface becomes more ordered and crystalline the emission of longer fragments from the thiol chains is reduced relative to the emission of short fragments. Thus PCA is extracting information about the interaction and energetics of the surface. Using the PCA trends, a multivariate ratio (SAMratio) was created. This ratio was applied to a completely different set of thiol SAMs of varying chain length and head group. A correlation was found between the SAMratio and the parachor of the surfaces. Therefore PCA analysis was able to determine real data trends that lead to insight into the TOF-SIMS fragmentation process and a direct correlation with a thermodynamic property of the surface. The ability to extract this type information has the potential to revolutionize TOF-SIMS analysis by unlocking the information within the TOF-SIMS fragmentation pattern that is not accessible from univariate analysis.

10:20am **MC-WeM7 Z-dol PFPEs on Magnetic Recording Disks: A PLS Study of TOF-SIMS Spectra**, ***A. Spool,*** *K. Kuboi, R. Waltman, P. Kasai,* IBM Corporation

Statistical methods were used to show how variations in the peak intensities in the TOF-SIMS spectra of Z-dol Perfluoropolyether (PFPE) lubricant deposited on magnetic recording disks vary with the properties of the lubricant. Partial Least Squares analysis of a large number of spectra successfully modeled variations in lubricant thickness, molecular weight and the ratio of the 2 main repeating units in the Z-dol copolymer. The peaks of most significance (largest absolute regression factor) for each model were then examined to relate fragment structures to the physical property being modeled. This in turn was used to further our understanding@footnote 1,2@ of the spectra themselves. @FootnoteText@ @footnote 1@ A. M. Spool and P. Kasai, Macromolecules 29, 1691 (1996). @footnote 2@ P. H. Kasai and A. M. Spool, J. Phys. Chem. B 102, 7331 (1998).

10:40am **MC-WeM8 Exploration of the Time-of-Flight Secondary Ion Mass Spectra of Combinatorially Designed Polyarylates by using a Novel Multivariate Statistical Approach**, ***B.J. Tyler,*** Montana State University*; A. Belu,* Physical Electronics

In this study, a novel multivariate data analysis method has been used to explore relationships in the TOF-SIMS spectra from a series of polyarylates, with well-controlled and systematically varying chemistry. A series of 16 polyarylates was prepared from 4 distinct tyrosine-derived dipheols and 4 aliphatic diacids. This series is a subset of a library of 112 polyarylates described by Brocchini et al. These materials which have well controlled and systematically varying chemistry are ideal for evaluation by surface analysis techniques. The effects of incremental increase in polymer backbone length and polymer side-chain length can be evaluated. SIMS spectra of these polymers have been investigated by Belu, et al. These polymers show a series of peaks which are shifted by a mass characteristic of the particular polyarylate chemistry. Although principal components analysis and other multivariate methods have proved to be a very powerful aid for interpreting SIMS spectra, patterns which are shifted by a mass unit are invisible to these methods. A novel approach to multivariate analysis has been developed which is sensitive to characteristic shifts in the mass spectra rather than solely to peak positions. Details of the multivariate method as well as results for the polyarylate polymer series will be presented. @FootnoteText@ @Footnote 1@Brocchini S, James K, Tangpasuthado V, Kohn J, JACS, 1997; 119(19): 4553-4554 @Footnote 2@Belu A, Brocchini S, Kohn J, Ratner B, Rapid Communications in Mass Spectrometry, in press.

Magnetic Interfaces and Nanostructures
Room 206 - Session MI+EL-WeM

Magnetic Semiconductors and Hybrid Structures I

Moderator: B. Jonker, Naval Research Laboratory

8:20am **MI+EL-WeM1 Characterizations of MBE Grown Single Crystal Ferromagnetic Ni@sub 2@MnGa Thin Films on (001) Ga@sub 1-x@In@sub x@As**, ***J.W. Dong***[1]*, J.Q. Xie, L.C. Chen, M.T. Figus, S. McKernan, C.J. Palmstrom,* University of Minnesota

Minimization of spin flip scattering at the interface of ferromagnetic metal/semiconductor is expected with the use of high quality epitaxially grown ferromagnetic metal/semiconductor heterostructures with minimal interfacial reactions. The Heusler alloy Ni@sub 2@MnGa is ferromagnetic at room temperature and has the cubic L2@sub 1@ Heusler structure with lattice parameter 3% larger than that of GaAs. We have demonstrated MBE growth of 900 Å-thick single crystal Ni@sub 2@MnGa on (001) GaAs with a 6 monolayer-thick Sc@sub 0.3@Er@sub 0.7@As interlayer, which acts as a template layer and a diffusion barrier. Reflection high energy electron diffraction, X-ray diffraction, and transmission electron microscopy (TEM) studies confirm the single crystal structure of the Ni@sub 2@MnGa films and indicate that the growth is pseudomorphic on GaAs substrates. These results suggest an epitaxially stabilized tetragonal phase of Ni@sub 2@MnGa with a = b = 5.65 Å, c = 6.12 Å, which has not been found in the bulk. High resolution cross section TEM image shows that the interface between Ni@sub 2@MnGa films and the Sc@sub 0.3@Er@sub 0.7@As interlayer is atomically abrupt. The Rutherford backscattering channeling minimum yield of 6.5% further confirms the high quality of the Ni2MnGa films. At room temperature, magnetic measurements using a vibrating

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[1] **Falicov Student Award Finalist**

sample magnetometer show that the films are ferromagnetic with a coercivity of ~50 Oe, a saturation magnetization of ~250 emu/cm@super 3@, and a weak in-plane magnetic anisotropy. Using a superconducting quantum interference device magnetometer, the Curie temperature of the films is found to be ~340 K. Our results indicate that Ni@sub 2@MnGa/GaAs can form high quality ferromagnetic metal/semiconductor heterostructures that might be used for spin injection measurements. In this talk, the effect of interlayer and strain on the structural and magnetic properties of Ni@sub 2@MnGa on Ga@sub 1-x@In@sub x@As substrates will be discussed.

8:40am **MI+EL-WeM2 Molecular Beam Epitaxial Growth of Ferromagnetic Ni@sub 2@MnGe on GaAs(001)***, **J. Lu**, J.W. Dong, J.Q. Xie, D. Carr,* University of Minnesota*; V. Godlevsky,* Rutgers University*; C.J. Palmstrom,* University of Minnesota

A number of Heusler (L2@sub 1@) structures such as Ni@sub 2@MnX (X = Ga, In, Sn, Sb) are ferromagnetic shape memory alloys. The ferromagnetic Heusler alloys show promise as single crystal ferromagnetic spin polarized injecting contacts to semiconductors. In this work, epitaxial thin films of the Heusler alloy Ni@sub 2@MnGe have been for the first time grown on GaAs(001) substrate by molecular beam epitaxy (MBE). A two step growth procedure was used which included alternate layer epitaxy at 200°C of a thin Ni@sub 2@MnGe template layer followed by codeposition at 250°C. A (2x2) surface reconstruction was observed by in-situ reflection high energy electron diffraction. X-ray diffraction studies show that the Ni@sub 2@MnGe film is epitaxially grown on GaAs(001) with the crystallographic relationship: (001)@sub Ni2MnGe@//(001)@sub GaAs@, (110)@sub Ni2MnGe@//(110)@sub GaAs@ . X-ray diffraction was used to determine both the out of plane and in plane lattice parameters. These confirmed that the film had a tetragonal structure, with a = 5.65 ±0.02 Å c = 5.897 Å, and c axis perpendicular to film surface, suggesting pseudomorphic growth on the GaAs surface. The magnetic properties were measured using superconducting quantum interference device magnetometry (SQUID). The coercivity of the film is ~50 Oe, and the saturation magnetization Ms is ~ 200 emu/cm3. The Curie temperature was 330 ± 10 K. In this talk, the magnetic and structural properties of Ni@sub 2@MnGe/GaAs heterostructures as a result of growth procedures and composition will be discussed. Results from Rutherford backscattering and transmission electron microscopy studies will be correlated with the magnetic properties.

9:00am **MI+EL-WeM3 Demonstration of Electrical Spin Injection: The Spin-LED@footnote 1@***, **Y.D. Park**, B.R. Bennett, B.T. Jonker,* Naval Research Laboratory*; H.-D. Cheong, G. Kioseoglou, A. Petrou,* SUNY, Buffalo

Electrical spin injection into a semiconductor is a prerequisite for realizing the potential of semiconductor-based spintronic devices. This has been an elusive goal, however, and only modest effects (@<=@ 1%) have been obtained. We report here highly efficient electrical spin injection from a magnetic contact into a GaAs quantum well-based light emitting diode (LED) heterostructure (a spin-LED@footnote 2,3@) in which the spin injection efficiency exceeds 50%. Radiative recombination of spin polarized carriers in quantum wells results in the emission of circularly polarized light. The degree of optical polarization is proportional to the carrier spin polarization, enabling a direct, quantitative measure of the spin injection efficiency. The samples consist of ZnSe/ZnMnSe/AlGaAs/GaAs/AlGaAs heterostructures grown by MBE on p-GaAs(001) substrates, where the semimagnetic semiconductor ZnMnSe serves as a source of spin-polarized electrons which are injected via an applied bias voltage into the GaAs quantum well. Standard optical lithography and chemical etch procedures were used to define surface emitting LED mesa structures. The measured circular polarization of the electroluminescence (EL) exceeds 50%, and demonstrates that highly efficient spin transport occurs across the ZnMnSe/AlGaAs interface despite the large 0.5% lattice mismatch. Data are reported as a function of injection current, magnetic field, and temperature. The EL lineshape consists of multiple components whose relative polarization provide insight into spin relaxation mechanisms. We compare results from ex situ and in situ contacts, and with those obtained for carefully lattice matched systems.@footnote 4@. @FootnoteText@ @footnote 1@ This work was supported by the Office of Naval Research. @footnote 2@ US patent #5,874,749 (filed 6/93; awarded 2/99) @footnote 3@ Jonker, et al., submitted for publication. @footnote 4@ Fiederling, et al., Nature 402, 787 (16 December 1999).

9:20am **MI+EL-WeM4 Ferromagnetism and Spin Related Phenomena in Semiconductor Heterostructures***, **H. Ohno**,* Tohoku University, Japan **INVITED**

Alloys between non-magnetic III-V semiconductors and Mn have been grown by molecular beam epitaxy and shown to exhibit ferromagnetism at reduced temperatures. These alloys, (Ga,Mn)As, (In,Mn)As, and (Ga,Mn)Sb are quasi-lattice matched to their host semiconductors and thus offer new and unique opportunities to combine ferromagnetism and high quality III-V heterostructures being widely used in frontiers of semiconductor physics and also in commercially available devices. This talk covers the following topics: (1) Preparation and properties of ferromagnetic semiconductors, particularly (Ga,Mn)As, where transition temperature can be as high as 110 K for 5% Mn concentration.@footnote 1@ (2) The origin of carrier-induced ferromagnetism based on a mean field theory using kp approximation.@footnote 2@ (3) Ferromagnet/non-magnet tri-layer semiconductor structures exhibiting inter-layer magnetic coupling and spin-dependent scattering.@footnote 3@ (4) Resonant tunneling structures with ferromagnetic emitters.@footnote 4@ (5) Spin-injection experiments using ferromagnetic semiconductor heterostructures.@footnote 5@ (6) Spin relaxation in nonmagnetic (110) GaAs quantum wells, where prolonged spin relaxation times are observed,@footnote 6@ which can be over 10 ns from room temperature down to 5 K when modulation doped. @FootnoteText@ @footnote 1@ H. Ohno, Science, 281, 951 (1998), J. Mag. Mag. Materials, 200, 110 (1999). @footnote 2@ T. Dietl, H. Ohno, F. Matsukura, J. Cibert, and D. Ferrand, Science, 287, 1019 (2000). @footnote 3@ N. Akiba, D. Chiba, K. Nakata, F. Matsukura, Y. Ohno, and H. Ohno, J. Appl. Phys., 87, 6436 (2000). @footnote 4@ H. Ohno, N. Akiba, F. Matsukura, A. Shen, K. Ohtani, and Y. Ohno, App. Phys. Lett., 73, 363 (1998). @footnote 5@ Y. Ohno, D. K. Young, B. Beschoten, F. Matsukura, H. Ohno, and D. D. Awschalom, Nature, 402, 790 (1999). @footnote 6@ Y. Ohno, R. Terauchi, T. Adachi, F. Matsukura, and H. Ohno, Phys. Rev. Lett., 83, 4196 (1999).

10:00am **MI+EL-WeM6 Properties of Mn@sub x@Ge@sub 1-x@, Cr@sub y@Ge@sub 1-y@ and Mn@sub x@Cr@sub y@Ge@sub 1-x-y@ Semiconductor Films Grown by Molecular Beam Epitaxy@footnote 1@***, **J.E. Mattson**,* Naval Research Laboratory, US*; Y.D. Park, T.F. Ambrose, A.T. Hanbicki, A. Wilson, G. Spanos, B.T. Jonker,* Naval Research Laboratory

Mn doped GaAs exhibits ferromagnetic ordering along with semiconducting behavior.@footnote 2,3@ Recent theory@footnote 4@ suggests that low concentrations of Mn (10@super 20@ cm@super -3@). We describe here the structural, magneto-transport, and magnetic properties of Ge@sub 1-x@Mn@sub x@, Ge@sub 1-y@Cr@sub y@ and Ge@sub 1-y-x@Cr@sub y@Mn@sub x@ thin films (with x < 0.15, and y < 0.15) in which Mn and Cr act as acceptors. Samples were grown by MBE on GaAs(001) and Si(001) substrates at substrate temperatures ranging from 175 to 350°C and growth rates of 4-5 Å/min. For all growth conditions studied, the GeMn films show a largely diffuse RHEED pattern and lack of structural order as determined by XRD. The temperature dependence of the resistivity shows non-metallic behavior with room temperature hole concentrations as high as 3x10@super 20@cm@super -3@. The magnetic properties determined from SQUID magnetometry are similar to those of Ge@sub 8@Mn@sub 11@ bulk alloys, suggesting the formation clusters of Ge@sub 8@Mn@sub 11@ rather than a homogeneous alloy. Plan-view TEM confirms the presence of clusters. The GeCr films exhibit single crystal growth and are p-type with p

10:20am **MI+EL-WeM7 Characterizations of Fe Thin Films on GaAs (001) Grown at Cryogenic Temperatures by Molecular Beam Epitaxy***, **Y. Chye**, P Petroff,* University of California, Santa Barbara

One of our research objectives is to fabricate hybrid structures by integrating ferromagnetic materials into semiconductors. It has been demonstrated that molecular beam epitaxy (MBE) can be used to fabricate single crystalline Fe directly upon GaAs.@footnote 1@ However, the intermixing between Fe and GaAs at the interface forms a "magnetically dead layer"@footnote 1@ which will badly affect polarized transport and thus make efficient "spintronics" devices hard to realize. In an effort to circumvent this problem, we propose to grow Fe on GaAs at cryogenic temperatures (below -100 ° C). At these temperatures, the deposited Fe atoms and the GaAs surface atoms are less likely to react with each other through interdiffusion. To implement these ideas, we grow Fe thin films on GaAs (001) semi-insulating substrates at -150 ° C in an EPI-620 MBE with a liquid-nitrogen cooled sample stage. It is indicated by the streaky RHEED pattern that single crystalline Fe is grown on GaAs. The surface morphology, interface properties, crystal structure, film orientation and magnetic behavior of the samples have been characterized by atomic force microscopy (AFM), transmission electron microscopy (TEM), x-ray diffraction, and superconductivity quantum interference device (SQUID), respectively. To examine the interdiffusion at the interface, we perform photoluminescence (PL) measurements for samples with very thin Fe films grown at different temperatures above GaAs quantum wells. Our results show that the PL peaks for the quantum wells do not significantly change for the cryogenic temperature grown samples, whereas the room temperature grown samples show a dramatically reduced luminescence efficiency and energy emission shift. These results suggest that the cryogenic temperature deposition strongly suppress the interdiffusion between the Fe and GaAs at the interface. @FootnoteText@ @footnote 1@ J. J. Krebs, B. T. Jonker, G. A. Prinz, J. Appl. Phys., 61 (1987) 2596.

10:40am **MI+EL-WeM8 Growth and Magnetic Properties of Epitaxial Fe-N Films@footnote 1@**, ***F. Liu***, *S.-C. Byeon, C. Alexander, G.J. Mankey,* University of Alabama

Reported values of magnetic moments in epitaxial Fe@sub 16@N@sub 2@ films vary from 2.3 to 3.5 Bohr magnetons per atom.@footnote 2@ These discrepancies arise from the fact that the films are multiphase mixtures which decompose upon heating.@footnote 3@ To study this problem, 40 nm thick Fe-N films were produced using reactive sputtering in an ultra clean sputtering system with in situ RHEED. First, an S-terminated GaAs surface is prepared by wet chemical etching. After annealing at 450 C, a 3 nm thick Fe seed layer is deposited to promote epitaxial growth of a 20 nm thick Ag(100) buffer layer. The Fe-N film is then grown on this Ag(100) buffer. The sputtering power, Ar + N@sub 2@ pressure, and the substrate temperature were varied systematically to produce the optimal RHEED pattern. The films were capped with a 5 nm thick Ru layer for ex situ structural and magnetic analysis. XRD is used to identify the degree of N-site ordering and the unit cell volume. XPS depth profiling is used to determine the chemical composition of the Fe-N film. The structural and chemical measurements are correlated with ferromagnetic resonance and vibrating sample magnetometry measurements of the saturation magnetic moment. These results are used to clarify the origin of the "giant magnetic moment" in the ordered Fe@sub 16@N@sub 2@ phase. @FootnoteText@ @footnote 1@Funded by ARO #DAAH 04-96-1-0316 and NSF #DMR-9809423. @footnote 2@G.W. Fernando et al., Phys. Rev. B 61, 375(2000). @footnote 3@ Migaku Takahasi and H. Shoji, J. Magn. Magn. Mater. 208, 145(2000).

MEMS
Room 309 - Session MM-WeM
Microfabricated Sensors

Moderator: C. Zorman, Case Western Reserve University

8:20am **MM-WeM1 Microfabricated Platform for Semiconducting Metal Oxide Thin Film Gas Sensors**, ***D.J. Frankel,*** *C. Silvestre, G. Bernhardt, S.C. Moulzolf, N. LeCursi, R.J. Lad,* University of Maine

A sensor platform for chemiresistive and impedance based thin film gas sensors has been developed which can be fabricated using conventional microfabrication techniques. The platform utilizes a highly polished sapphire substrate with platinum electrodes, heater element, and resistance temperature detector (RTD). The use of highly polished and well characterized sapphire substrates allows controlled growth of thin metal oxide sensing films, yielding reproducible and well-defined microstructures. Techniques have been optimized that allow for more than 400 sensing devices to be fabricated on 3" diameter sapphire substrates using liftoff technology. Delamination of metallization on the sensor platform can be problematic, particularly following high temperature annealing. Strong adhesion between the platinum electrodes and sapphire substrate is achieved with a thin Zr adhesion layer. Adhesion is such that parallel gap welding of 4 mil Pt wire can be successfully obtained with bond strengths exceeding 100 grams force. Strong bonding is achieved after fabrication and following extended anneals up to 500C. These anneals are required to stabilize the resistance of the RTD and heater elements. The platform materials exhibit stable operation after accelerated temperature cycling between room temperature and the typical sensor operation temperature of 200-400C. We have also used microfabrication techniques to fabricate sensor platforms with a variety of electrode configurations, including under and on top of the metal oxide sensing film, that explore the effect of sensor resistance measurement configuration on sensor operation while keeping substrate effects constant.

8:40am **MM-WeM2 The Use of Micromachined Arrays to Develop Processing/Performance Databases for Metal/Oxide Sensing Materials**, ***J.E. Tiffany***, *R.E. Cavicchi, S. Semancik,* National Institute of Standards and Technology

We describe the efficient study of multiple metal/oxide microsamples on micromachined platforms called microhotplate arrays. These platforms include addressable temperature control of 36 individual elements which is employed in fabricating and evaluating varied sensing films being examined for solid state conductometric gas microsensors. Each 100 micron array element consists of a suspended structure with a buried heater and surface electrodes. We present results of screening experiments (metal coverage and type, annealing and sensing temperature, gas type) designed to generate a response database of sensitivity and selectivity. Tin oxide was deposited on all array elements via a Ni seeded, self-lithographic MOCVD process. Low coverage (25-100 Å) catalytic metal s (Ni, Pd, Pt, Cu, Ag, Co, Rh, Ir, Ru) were then deposited on select elements using masked evaporation or sputtering. We describe the response of these array elements to a wide variety of gases (2-butanone, acetone, toluene, benzene, methanol, ethanol, hydrogen, and carbon monoxide). Response data was collected for bare and catalyst modified sensors. The bare tin oxide films showed a normally distributed (10%) conductance response when exposed to the test gases at fixed temperature, demonstrating the statistical stability of the screening approach. Relative sensitivities for the different metal catalysts are reported as a function of sensing temperature for each test gas. We observed, for example, that the addition of Ni catalyst decreased hydrogen response, whereas 2-butanone response was increased. Benzene response was also observed to cross over from negative to positive at a specific temperature due to competing surface reactions both with and without Ni catalyst. Such cases of increased sensitivity, selectivity and crossover response can be extracted from the materials screening response data and be used in customizing microsensors for specific tasks.

9:00am **MM-WeM3 Chemical Detection Based on Adsorption-Induced and Photo-Induced Stresses in MEMS Devices**, *P.G. Datskos, S. Rajic, L.R. Senesac,* Oak Ridge National Laboratory; ***I. Datskou,*** Environmental Engineering Group, Inc.; *M.S. Sepaniak, C.A. Tipple, B.C. Fagan,* University of Tennessee

Recently there has been an increasing demand to perform real-time in-situ chemical detection of hazardous materials, contraband chemicals, and explosive chemicals. Currently, real-time chemical detection requires rather large analytical instrumentation that are expensive and complicated to use. The advent of inexpensive mass produced MEMS (micro-electro-mechanical systems) devices opened-up new possibilities for chemical detection. For example, microstructures were found to respond to chemical stimuli by undergoing changes in their bending and resonance frequency even when a small number of molecules adsorb on their surface. In our present studies, we extended this concept by studying changes in both the adsorption-induced stress and photo-induced stress as target chemicals adsorb on the surface of microstructures. For example, microstructures that have adsorbed molecules will undergo photo-induced bending that depends on the number of absorbed molecules on the surface. However, microstructures that have undergone photo-induced bending will adsorb molecules on their surfaces in a distinctly different way. Depending on the photon wavelength and microstructure material, the microstructure can be made to bend by expanding or contracting the irradiated surface. This is important in cases where the photo-induced stresses can be used to counter any adsorption-induced stresses and increase the dynamic range. Coating the surface of the microstructure with a different material can provide chemical specificity for the target chemicals. However, by selecting appropriate photon wavelengths we can change the chemical selectivity due to the introduction of new surface states in the MEMS device. We will present and discuss our results on the use of adsorption-induced and photo-induced bending of microstructures for chemical detection.

9:20am **MM-WeM4 Optical Emission Study of a Microfabricated Inductively Coupled Plasma**, ***O. Minayeva,*** *J.A. Hopwood,* Northeastern University

Recently, the fabrication@footnote 1,2@ and characterization@footnote 3,4@ of a micromachined 5-mm inductively coupled plasma (ICP) generator was reported. One of the applications for a microplasma source is the detection of gaseous impurities in air using a micromachined Fabry-Perot interferometer to monitor the optical emissions of the plasma. In this work the complete system that includes a microplasma generator, vacuum chamber, optical path, and lab-scale spectrometer was built and tested on several gas discharges. The goal was to maximize the electronic excitation reaction followed by the light emission from a toxic gas sample (e.g., SO@sub 2@) diluted in air (or argon). It was found that an electron temperature of ~3 eV favors the excitation reaction for SO@sub 2@. The chamber was designed to provide this value of electron temperature over an operating pressure of 0.5-1 torr. Optical paths were incorporated in the chamber in order to collimate the plasma's light emission to within 3-4@super o@ prior to filtering and detection by the interferometer. Multiple optical paths also allow one to determine the spatial structure of the plasma. The optical emission spectra were taken at different points within the micro ICP, and the results on light intensity distribution across the discharge will be presented. @FootnoteText@ @footnote 1@ J. Hopwood, "Monolitic miniaturized inductively coupled plasma source;" U.S. Patent No. 5,942,855 (August 24, 1999). @footnote 2@ Y. Yin, J. Messier, and J. Hopwood, "Miniaturized inductively coupled plasma sources," IEEE Transactions on Plasma Science, 27(5), 1516-1524, (1999). @footnote 3@ J. Hopwood, O. Minayeva, Y. Yin, "Fabrication and characterization of a micromachined 5-mm inductively coupled plasma generator," submitted to J. Vac. Sci. Technol. @footnote 4@ J. Hopwood, "A microfabricated inductively-coupled plasma generator," submitted to J. Microelectromechanical Systems.

9:40am **MM-WeM5 A Micromachined Scanning Fabry-Perot Interferometer***, **F.C. LI,*** Northeastern University, U.S.A*; N.E. McGruer,* Northeastern University*; P.M. Zavracky, K.L. Denis,* Northeastern University, U.S.A

This work describes a novel process to fabricate a micromachined scanning Fabry-Perot interferometer (FPI) employing electrostatic actuators. The Northeastern University MEtal Micromachining (NUMEM) is used to build the electrostatic actuators, which consist of four free standing gold cantilever beams. Two highly reflective mirrors are fabricated separately. @footnote 1@ The final assembly step bonds the upper mirror to the beams and completes the device. The two plane parallel mirrors are initially separated by a gap of approximately 600nm. By applying appropriate control voltages between the beams and electrodes on the substrate, the device can be tuned to wavelengths in the visible spectrum from 450 to 750 nm. Four sense capacitors are placed underneath the upper mirror to detect the spacing between the two mirrors. The spacing information is supplied to a closed-loop control circuit which scans the upper mirror vertically and maintains parallelism. Devices fabricated with aluminum mirrors (reflectivity approximately of 85%) showed resolving powers of 26, 24 and 18.2 at the wavelengths of 525nm, 615nm and 660nm, respectively. Proposed applications of the micromachined FPI include in situ measurements of plasma composition, colorimetric, and chemical analysis. @FootnoteText@ @footnote 1@ P.M. Zavracky, K.L. Denis, H.K. Xie, T. Wester and P. Kelly, "A Micromachined Scanning Fabry-Perot Interferometer", Proceedings of SPIE-The International Society for Optical Engineering, v 3514 p 179-187, Sep 21-22, 1998.

10:00am **MM-WeM6 Passivation of MEMS Structures that are Integrated with Support Electronics***, **J.R. Martin,*** Analog Devices Inc. **INVITED**

MEMS devices are susceptible to surface conditions because they are seldom passivated. For example, electrical and optical performances are affected when unpassivated surfaces adsorb or chemically react with ambient gases. Stiction can occur if shock impacts cause these high-energy surfaces to touch. Unfortunately, it is difficult to passivate MEMS wafers due to microstructure flatness requirements, metal temperature limitations and surface charging during low temperature plasma processes. Some SAM coatings are reasonable candidates. However, organics do not normally survive the cerpac process used to package ADXL accelerometers (several furnace passes in air at 430-450C). This presentation will describe a new MEMS passivation process based on a custom synthesized diphenyl siloxane. Organics with the best thermo-oxidative resistance contain phenyl rings so vapor deposited diphenyl siloxane films were evaluated on polysilicon accelerometers. Silicones (molecules with a silicon oxide backbone) were used to transport and bond phenyl rings to the sensor surface. As a result, the native oxide is modified by formation of a low-energy (organic-rich) surface that survives the packaging process. This approach also minimizes contamination concerns because any degradation products are essentially identical to the native oxide that already exists on polysilicon surfaces. A variety of deposition conditions and two types of equipment were evaluated for both electrical and stiction characteristics. Varying the type of diphenyl siloxane caused large differences in anti-stiction performance. Control of the final process is impressive. For example, 100 wafer coating runs have a thickness uniformity of +/- one angstrom. There is no practical way to measure coatings on MEMS surfaces with this level of precision. Therefore, specially prepared monitor wafers are placed in each furnace boat. Early results show that run to run uniformity is also in the +/- one angstrom range.

Processing at the Nanoscale/NANO 6
Room 302 - Session NS+NANO6+MC-WeM

Nanomechanical and Interface Measurements

Moderator: R.J. Hamers, University of Wisconsin, Madison

8:20am **NS+NANO6+MC-WeM1 Surface Acoustic Wave Investigation by UHV Scanning Tunneling Microscopy***, **P.U. Voigt**, S. Krauß, E. Chilla, R. Koch,* Paul-Drude-Institut für Festkörperelektronik, Germany

Recently we have shown that the scanning tunneling microscope can also be used to investigate surface acoustic waves (SAW) of 35 MHz by adding a high frequency sinusoidal signal to the dc tip voltage.@footnote 1@ Due to mixing with the SAW oscillation at the tunneling gap the tunneling current contains both amplitude and phase information of the SAW. Here we report on the first UHV compatible version of this technique including provisions for sample transfer and in situ surface preparation. Since both signal-to-noise ratio and spacial resolution are significantly enhanced, the acoustic oscillation of single atoms and monoatomic steps can be investigated. At present SAW frequencies up to 500 MHz have been successfully fed into the UHV system. @FootnoteText@ @footnote 1@ E. Chilla, W. Rohrbeck, H.-J. Fröhlich, R. Koch, K. H. Rieder, Appl. Phys. Lett.61, 3107 (1992) .

8:40am **NS+NANO6+MC-WeM2 Q-Control: Characterizing Highly Sensitive Surface Structures with the AFM***, **B. Anczykowski,*** NanoAnalytics WWU Münster, Germany*; L.F. Chi, H. Fuchs,* Physikalisches Institut WWU Münster, Germany

When operating an atomic force microscope (AFM) in a dynamic mode the oscillation of the cantilever is influenced by non-linear interaction forces between the probing tip and the surface. In principle the instantaneous forces exerted on the sample while scanning the surface can be either repulsive or attractive. Experimental findings and corresponding computer simulations of the tapping mode show that by choosing appropriate system parameters the AFM can continuously be operated in the regime of net-attractive interaction forces. Thereby the risk of modifying the sample surface by the probing tip is minimized. However, in most cases the range in which the system parameters have to be adjusted is rather narrow and therefore a stable operation of the AFM in this interaction regime is difficult to achieve. With the help of the Q-Control module it is possible to reduce the damping of the dynamic system, i.e. to increase the effective quality factor of the oscillating cantilever and thereby to enlarge the regime of net-attractive interaction forces.@footnote 1@ This method allows to minimize the forces exerted by the probing tip on the sample surface. Therefore by applying Q-Control delicate and highly sensitive surfaces, such as ultrathin organic layers or DNA structures, can be characterized with high resolution. @FootnoteText@ @footnote 1@B. Anczykowski, J. P. Cleveland, D. Krüger, V. B. Elings, and H. Fuchs, Appl. Phys. A 66, S885 (1998).

9:00am **NS+NANO6+MC-WeM3 Traceability for Nanoscale Properties***, L.P. Howard, **J. Pratt,*** National Institute of Standards and Technology **INVITED**

The accuracy of nanoscale materials properties measurements ultimately depends upon the accurate determination of many SI units. When measurements are pushed into the nano-scale, many difficult circumstances arise due to what may be effectively described as a poor signal to noise ratio. This talk will highlight work involving the integration of interferometers into scanned-probe microscopes and work in traceable, sub-micronewton force measurements. Interferometry provides us the means to realize the meter. Several applications of sub-nanometer laser interferometry will be presented in the context of scanned-probe microscopes. Atomic lattice spacings have been measured using interferometers, and the expanding role of the atomic lattice in scanned-probe microscope metrology will be explored. Nanonewton force measurements are the subject of a new NIST project with the goal of improving traceability below the micronewton level. The unit of force is derived from the SI base units. Extending force measurement accuracy to the nanonewton level can require a combination of difficult dimensional, mass and electrical measurements. Our development of an electromagnetic balance capable of interfacing to scanned-probe instruments will be highlighted. With this new instrument (and a related electrostatic balance), we will explore the practical limits of using an electrical representation of the newton while attempting to extend our traceability chain back to a purely mechanical realization of force using mass and the earth's gravitational acceleration.

9:40am **NS+NANO6+MC-WeM5 Low Temperature Scanning Force Microscopy of the Si(111) 7x7 Surface and Site-specific Measurements of Tip-Sample Interaction Forces***, **M.A. Lantz**, H.J. Hug, S. Martin, A. Abdurixit, A. Baratoff, R. Hoffmann, P. Kappenberger, P.J.A. van Schendel,* University of Basel, Switzerland*; Ch. Gerber,* IBM Research Division, Zuerich Research Laboratory*; H.-J. Guentherodt,* University of Basel, Switzerland

A low temperature scanning force microscope (SFM) operating in a dynamic mode in ultra high vacuum was used to study the Si(111)7x7 surface at 7.2K. Not only the twelve adatoms but also the six rest atoms of the unit cell are clearly resolved for the first time with SFM. In addition, the first measurements of the short-range chemical bonding forces above specific atomic sites are presented. The data is in good agreement with first-principles computations and indicates that the nearest atoms in the tip and sample relax significantly when the tip apex is within a few Å of the surface.@footnote 1@ New experiments with non-reactive tips reveal atomically resolved images with surprisingly different contrast from those obtained with a reactive tip. Careful analysis of frequency and damping versus distance curves clearly shows the obtained contrast does not result from the formation of a covalent bond, however atomic resolution is still obtained. This strongly suggests that true atomic resolution can be obtained with a new type of tip-sample interaction.The physical nature of this interaction mechanism will be discussed and compared to theoretical models.@FootnoteText@@footnote 1@Lantz et al., Phys. Rev. Lett 84, 2642 (2000).

10:00am **NS+NANO6+MC-WeM6 Simultaneous STM/nc-AFM Imaging and Force Spectroscopy of Si(100)-(2x1) Surface with Small Oscillation Amplitudes***, **H.O. Ozer**, A. Oral,* Bilkent University, Turkey*; J.B. Pethica,* University of Oxford, UK

We have used a new, fiber interferometer based, high force resolution nc-AFM to image the Si(100)(2x1) surface with atomic resolution, using very small tip oscillation amplitudes down to 0.5 ?pp. The lever is dithered with the small oscillation amplitude at a frequency below resonance and the changes in the oscillation amplitude recorded simultaneously with force gradient and STM topography. With this method we can measure the force gradients quantitatively. Simultaneous images of Force gradient and STM topography have been recorded as a function of tunnel current and bias voltage. The effect of tunnel current and bias voltage on the force gradient contrast will be presented. We have also present force-distance curves between tip and Si(100) surface, measured with sub-Angstrom oscillation amplitudes.

10:20am **NS+NANO6+MC-WeM7 A Liquid Helium Temperature Ultrahigh Vacuum Dual-tip Scanning Tunneling Microscope***, **H. Okamoto**, D. Chen,* Rowland Institute for Science

A dual-tip scanning tunneling microscope (D-STM) is a powerful instrument for investigating dissipative, diffusive, or ballistic transport phenomena of electrons in nanoscale structures.@footnote 1@ Here we present an ultrahigh vacuum compatible D-STM system working at liquid helium temperature for these new potential applications. Coarse positioning system consists of five rigid and compact inertial steppers, which has mechanical resonant frequency of ~900 Hz after integration. Each stepper has embedded capacitive position sensors with sub-micron resolution. An efficient new method, which we call tri-plane method, is used to navigate the two tips to proximity. The whole D-STM system is installed in a home-made vapor-cooled helium cryostat with a very low evaporation rate of 1.25 liter/day without liquid nitrogen radiation shield. @FootnoteText@ @footnote 1@Q. Niu et al., Phys. Rev. B 51 5502 (1995).

Organic Films and Devices
Room 313 - Session OF+EL+SS-WeM

Transport and Device Issues in Organic Thin Films

Moderator: A. Kahn, Princeton University

8:20am **OF+EL+SS-WeM1 The Transport and Injection of Positive Carriers in Conjugated Electroluminescent Polymers and their Devices***, **A.J. Campbell**,* University of Sheffield, UK, U.K.*; D.D.C. Bradley,* University of Sheffield, UK*; H. Antoniadis,* Infineon Technologies Corp. **INVITED**

Organic light emitting diodes (OLEDs) based on electroluminescent conjugated polymers are an important emerging technology with a wide range of display and lighting applications. Polyfluorene and its copolymers are considered to be amongst the most promising materials for use in commercial OLEDs. Indium tin oxide (ITO) is also the hole injecting electrode of choice in any practical device. Here we report the results of time-of-flight measurements on the transport of positive carriers in polyfluorene and its copolymers. The field and temperature dependence of the charge carrier mobility is compared to theoretical models for charge transport in disordered organic materials. We also report the results of dark injection and current density-voltage measurements on the injection of holes from differently prepared ITO contacts. The absolute injection efficiency of the contacts is calculated by comparison to trap-free, space-charge-limited current (TFSCLC). The injection efficiency is shown to vary with not only polymer ionisation potential but also with the nature of the ITO preparation (i.e. washed in solvents, exposed to an oxygen plasma, coated with a film of poly(ethylenedioxythiophene) / polystyrenesulphonic acid). The variation of the injection efficiency with temperature is also reported.

9:00am **OF+EL+SS-WeM3 Grain Boundary Effects on Electrical Transport in Polycrystalline Organic Semiconductor Thin Films***, **R.J. Chesterfield**, A.B. Chwang, K. Puntambekar, C.D. Frisbie,* University of Minnesota

The role of microstructure in electrical transport in polycrystalline thin films of organic semiconducting oligomers (e.g., pentacene, sexithiophene) has not been extensively explored. This talk describes experiments in which transport through single grain boundaries (GBs) is probed using field effect transistor (FET) structures and Kelvin probe force microscopy (KPFM). In the FET studies, closely spaced gold source and drain electrodes are connected to pairs of pentacene or sexithiophene microcrystals grown on insulating substrates, such as SiO@sub 2@. The microcrystals, or grains, share a common boundary that dominates the transport through the FET. Conduction through the GB is measured as a function of gate field and temperature, and the results are compared with a recent model by Schon and Batlogg.@footnote 1@) In the KPFM studies, a metal-coated AFM tip is used to record potential distributions across an operating microcrystal FET. The resulting images reveal where the voltage is dropped across the device and thus point to the chief bottlenecks in the current transport. In general, both the microcrystal FET and Kelvin probe experiments show that microstructure, and in particular GBs, can potentially dominate transport in polycrystalline organic semiconductor films. @FootnoteText@ @footnote 1@J. H. Schon, B. Batlogg, Appl. Phys. Letters, 74(2), 1999, 260-262.

9:20am **OF+EL+SS-WeM4 Quantum Confinement and Electron Transfer at Organic-Metal Interfaces***, **G. Dutton**, H. Wang, X.-Y. Zhu,* University of Minnesota

Electron transfer at organic-metal interfaces is important in molecule-based electronic and optoelectronic devices, such as light-emitting devices (LEDs), field-effect transistors (FETs), and molecular quantum wires (QW). We probe interfacial electronic structure and electron transfer dynamics using two-photon photoemission in model systems: thin films of hexafluorobenzene and naphthalene adsorbed on Cu(111). Electron transfer to the lowest unoccupied molecular orbitals, as well as to those mixed with image-type states, are observed. In both systems, these resonances display quantum well behavior: the electronic wavefunction is delocalized parallel to the surface but confined in the direction normal to the surface. The detailed structure and dynamics are established by dispersion measurements and by femto-second time-resolved two-photon photoemission. We believe the formation of these molecular quantum wells is a result of the strong interaction of molecular states with the metal substrate. A simple theoretical framework is developed to describe the formation of these molecular quantum wells.

9:40am **OF+EL+SS-WeM5 Chemistry and Electronic Properties at Metals (Al, Mg and Au)-Organic Molecular Semiconductor (F@sub 16@CuPc) Interfaces***, **C. Shen**, J. Schwartz, A. Kahn,* Princeton University

The fabrication of efficient and stable metal-organic contacts is exceedingly important for the optimization of organic devices such as organic light emitting diodes (OLED) and thin film transistors. Al and Mg have low work functions and are typically used as electron injecting cathode materials. Au is a mostly inert metal in contact with organic materials. F@sub 16@CuPc is a candidate for n-channel thin film transistor material because of it relatively high electron mobility. Chemistry and physical processes (e.g. interdiffusion) that take place at metal/organic interfaces have a direct impact on the electronic properties of the contacts. It is generally believed that metals deposited on organics lead to more extensive interface chemistry and broader interfaces than organics deposited on metals. In some cases, these interfaces have actually been reported to lead to drastically different electrical behavior. The interfaces fabricated in ultra-high vacuum, however, shows identical electrical behavior.@footnote 1@ We have investigated the interface chemistry, electronic structure and electrical transport in nominally symmetric metal/F@sub 16@CuPc/metal structures fabricated and tested in ultra-high vacuum. For these structures, we performed detailed ultra-violet and X-ray photoemission spectroscopy (UPS, XPS) photoemission spectroscopy measurements that suggest that the chemistry at metal-on-organic interfaces is very similar to, if not identical with, that at organic-on-metal interfaces. Using current-voltage measurements performed in vacuum, we demonstrate that carrier injection is identical from top and bottom cathodes. @FootnoteText@ @footnote 1@Role of electrode contamination in electron injection at Mg:Ag/Alq@sub 3@ interfaces, C. Shen, I.G. Hill and A. Kahn, Adv. Mat. 11, 1523 (1999).

10:00am **OF+EL+SS-WeM6 Microcontacts to Self-Assembled Monolayers with a Conducting AFM Tip***, D.J. Wold,* ***C.D. Frisbie,*** University of Minnesota

Molecular level electrical transport studies require innovative approaches for making electrical contacts to oriented molecules. While scanning tunneling microscopy (STM) and electrochemical methods have been used for years to study transport in surface-confined molecules, conducting probe atomic force microscopy (CP-AFM) provides an alternative approach to electrically contacting monolayer films and the formation of metal-molecule-metal junctions. In CP-AFM, a metal-coated AFM tip is placed in direct contact, under controlled load, with the material to be probed. The technique differs from STM in that the probe is positioned using normal force feedback, which decouples probe positioning from electrical measurements. Using this technique, we show that CP-AFM may be used to make mechanically stable electrical contact to SAMs of alkane thiols on Au. We have probed the current-voltage (I-V) characteristics of the resulting junctions as a function of the number of methylenes in the alkane chains and the load applied to the tip-sample contact. The ease of this technique and the fine control of the probe during measurements make CP-AFM a promising approach for studying transport through molecular junctions. Further studies of dependence on conjugation, functional group distributions, orientations, and molecular dimensions will also be discussed.

10:20am **OF+EL+SS-WeM7 White-Light-Emitting Organic EL Devices Based on Vacuum Deposited Thin Films***,* ***J. Kido,*** Yamagata University, Japan **INVITED**

In this paper, we describe the design and fabrication of bright and high efficiency white-light-emitting EL devices based on vacuum deposited organic thin films. In order to archive high quantum efficiency, multilayer structures are employed. White light can be generated by using two emitter layers composed of blue and yellow emitters. For the blue emitter layer, distyrylbiphenyl derivative is doped with a few percent of distyrylarylene derivative with carbazolyl groups. For the yellow emitter layer, rubrene was doped into hole-transporting arylamine derivative (NPD). Reduction of drive voltage was realized by using metal-doped electron injection layer,@footnote 1@ which is composed of electron-transporting bathophenantroline (Bphen) doped with Cs metal. Cs-doping to Bphen reduces resistivity of the Bphen film, and the contact between cathode and the Bphen layer becomes ohmic, which results in the low drive voltage. The typical device structure is ITO/NPD/yellow-emitting layer/blue-emitting/Bphen doped with Cs/Al. By optimizing the thickness of each layer and dopant concentration, the white EL devices exhibited extremely high luminous efficiency of 15 lm/W and external quantum efficiency of 4% which are the highest values reported for white organic EL devices. @FootnoteText@@footnote 1@J.Kido and T.Matsumoto, Apply. Phys. Lett, 73, 2868(1998).

Plasma Science and Technology
Room 311 - Session PS+MS-WeM

Plasma-Induced Damage

Moderator: L.J. Overzet, University of Texas, Dallas

8:20am **PS+MS-WeM1 Plasma-Induced Charging Gate Oxide Pinhole Formation***,* ***T.C. Ang****, S.Y. Loong, P.I. Ong, W.B. Loh,* Chartered Semiconductor Manufacturing, Singapore*; Y.W. Teh,* Nanyang Technological University, Singapore

Plasma process induced charging damage to gate oxide is a growing concern in ULSI MOS device fabrication. This is due to gate oxide thinning resulting from continuous CMOS downsizing and increasing use of high density plasma (HDP) tools. In this paper, we study the extent of the plasma induced damage resulting from HDP inter-metal dielectric deposition process in 0.18um transistor technology. Gate oxide pinhole formation resulting from plasma induced charging damage was observed above a threshold ion density. Transistor test structures with different types of antennas and antenna ratios were used to monitor the plasma damage. The extent of the plasma charging damage was evaluated through shift in gate leakage, threshold voltage and transconductance from a reference transistor with no antenna attached. Each of these parameters were measured for a large number of transistors in order to statistically assess the level of plasma based gate oxide damage. Gate oxide pinhole formation was observed in transistors with antenna ratios above a certain value. The pinholes were caused by localized breakthrough of the gate oxide resulting from charge imbalance in the plasma and are only present when the charge imbalance exceeds a threshold value. Based on our results, we have determined the threshold value for charge imbalance and ion density to cause gate oxide pinhole formation. We have also developed a novel integration scheme which is effective in reducing the charging damage from the high density plasma process significantly and no gate oxide pinholes were observed with the implementation of this scheme.

8:40am **PS+MS-WeM2 Effects of Plasma-induced Charging Damages on Thin Gate Oxide during Plasma Etching Processes***,* ***Y.-K. Kim,*** *K.-O. KIm, J.-Y. Kim, C.J. Choi, J.W. Kim,* Hyundai Electronics Industries Co., Ltd., Korea

Using the plasma damage monitoring (PDM) system, we investigated the plasma-induced charging damage in the thermally-grown SiO@sub 2@ on p-type Si substrates after plasma etching of gate electrode. Recently, the technique has been frequently employed to monitor oxide damages induced by plasma processes. It determines the changes in oxide electrical properties such as flatband voltage (V@sub fb@), oxide resistivity (@rho@@sub ox@), effective charges (Q@sub eff@), interface trap density (D@sub it@), etc. The measured Q@sub eff@ as well as D@sub it@ value indicates that the plasma has induced a large amount of positive charges trapped in the bulk oxide and the interfacial defects in the SiO@sub 2@-Si interfaces. The trapped oxide charges are also the origin of the large V@sub fb@ shifts as well as the reduced @rho@@sub ox@. The observed charging damages have been found to be dependent strongly on the etching gases as well as the plasma conditions. The site-dependent variations of the charging damages were attributed to the non-uniform radial distribution of the charges on the oxide surfaces during the etching processes. A MOS capacitor was fabricated over the thin thermal oxide by employing the above plasma exposures during the poly-Si electrode and the subsequent pad etching to measure the changes in the gate oxide integrity (GOI) characteristics. Finally, we will quantitatively show that the leakage current of the thin gate oxide after the plasma processing is strongly related with the measured PDM results.

9:00am **PS+MS-WeM3 The Use of Simultaneous Modulation of Source and Wafer RF to Reduce Plasma Induced Damage***,* ***N. Hershkowitz,*** University of Wisconsin, Madison **INVITED**

A variety of different types of plasma phenomena can lead to plasma induced damage in the fabrication of small geometry devices. Oxide charging (probably the most significant source of damage), macroscopic and microscopic differential charging, over energetic ion beams, UV induced carriers and plasma etch induced silicon substrate roughness are some examples. In this paper, it is argued that simultaneous modulation of source and wafer RF in HDP tools provides a "control knob" for eliminating and/or reducing many of the sources of damage. Data are presented showing improvements resulting from simultaneous source and wafer (on-off) modulation. RF frequency and modulation duty cycle effects are discussed together with damage reduction mechanisms.

9:40am **PS+MS-WeM5 Effect of Oxide to Nitride Etch Selectivity on Plasma Induced Charging Damage***,* ***S. Ma****, C. Björkman, R. Wang, L. Zhang, H. Shan,* Applied Materials Inc.*; R. Ramanathan,* Conexant Systems

Nitride layers are widely used for dual-damascene, self-aligned contact and border-less contact dielectric etch process as etch stop layers. It is also believed that such etch stop layer on top of metal electrode can also serve as plasma charging damage protection layer. This study shows no relationship between the dielectric to nitride etch selectivity and plasma induced charging damage. A Magnetically Enhanced Reactive Ion Etching (MERIE) chamber is used for this study with 0.25 um technology devices. In fluorine contained etching chemistry, strong recipe dependence on plasma charging damage is found regardless of the dielectric to nitride etch selectivity. A model of leaky nitride with charge built up on via hole bottom is proposed to explain the phenomena. In pure oxygen chemistry for in-situ polymer removal, plasma induced charging damage depends on the remaining nitride thickness. It is found that power is the most sensitive parameter than B-field, pressure, overetch and gas species to control damage. A mechanism is also proposed to explain the role of polymer formation and removal on top of nitride stop layer to plasma charging damage sensitivity

10:00am **PS+MS-WeM6 Aspect Ratio Dependent Plasma-Induced Charging Damage in RF Pre-Cleaning of Metal Contact***, **J. Kim**, K.S. Shin, W.J. Park, C.J. Kang, T.-H. Ahn, J.-T. Moon,* Samsung Electronics, Korea

As the packing density increases in the fabrication of semiconductor, the aspect ratio and the CD (Critical Dimension) of a metal contact are exponentially aggravated in the dry etch process. The aspect ratio dependency on a plasma-induced charging damage during the RF pre-cleaning of a metal contact has been evaluated with the two dimensional Monte-Carlo simulation and the related experiments. From the simulation of a metal contact opened on a gate metal, it is found that the potential on a metal contact bottom, which is directly related to plasma-induced charging damage, is saturated near 4 of aspect ratio after linearly increasing with the aspect ratio. However, the linear decrease of CD of a metal contact exponentially increases the potential stress on gate oxide. These simulation results are confirmed with the two different experiments, an in-situ charge-up monitoring and the electric test of a fully fabricated CMOS wafers. A phase-controlled inductively coupled plasma is proposed to suppress the plasma-induced charging damage. With the phase-controlled inductively coupled plasma, the plasma-induced damage is strongly suppressed when the phase delay of the bias power to the source power is near 180 degree.

10:20am **PS+MS-WeM7 Real-time Observation of Relaxation of Disorder-induced Surface Stress***, **T. Narushima**, N. Ueda,* University of Tsukuba, Japan*; A.N. Itakura,* National Research Institute for Metals, Japan*; T. Kawabe,* University of Tsukuba, Japan*; M. Kitajima,* National Research Institute for Metals, Japan

We present relaxation of disorder-induced surface stress. The surface stress changes on Si(100) were measured by means of an optical micro-mechanical cantilever technique. The samples were Si(100) cantilevers (450µm x 50µm x 2µm). They were treated by being dipped in 10% HF acid solution for 5 minutes, rinsed with deionized water for 5 minutes, and annealed at 1000K for 30 minutes in a UHV. To introduce disorder to surface, the surfaces were bombarded using an argon plasma with applying negative biases (-30V to -100V) at room temperature. Then, the disordered surfaces were oxidized using an oxygen plasma with applying positive bias (+45V), where the surfaces were subject to electron irradiation. We found a development of compressive stress on the Si surface due to defects produced by ion bombardment. This disorder-induced compressive stress was completely relaxed by the following plasma oxidation. The initial evolution of the surface stress during oxidation on the bombarded surfaces is quite different from that on unbombarded Si(100) surfaces. The disorder-induced stress was also relaxed completely by an exposure to argon plasmas under anodic conditions. The stress relaxation should be promoted not only by oxidation but also by electron irradiation. A possible mechanism of the stress relaxation is surface diffusion of Si adatoms via electron irradiation.

10:40am **PS+MS-WeM8 Transient Charging Effects of Insulating Surfaces Exposed to a Plasma During Pulse Biased DC Magnetron Sputtering.***, **E.V. Barnat**, T.-M. Lu,* Rensselaer Polytechnic Institute

The ability to control the charging of thin dielectric films exposed to ionized discharges, using a pulsed bias, is studied experimentally and theoretically. A dielectric film is exposed to the discharge and the transient currents associated with the dielectric's charging are measured after each pulse. Factors effecting the time scale the film undergoes charging, including the dielectric constant, the dielectric's thickness, the plasma density, and the amount of potential applied during each pulse are explored. By constructing a simple model based on the plasma's impedance to the pulsed bias and the capacitive coupling between the electrode and the surface of the dielectric where the charge accumulates, the observed transient currents are explained. Calculations are then made to determine the energy distribution of the ions extracted from the plasma and how both the pulse of the electrode and the charging of the dielectric influence the ion energy distributions. To demonstrate an application of the pulse bias technique, it is shown that we can dramatically control the film morphology and microstructure by pulse biasing the electrode. Also, by properly setting the pulse bias, the pulse frequency or the pulse duty, damage to thin dielectric films, such as electrical breakdown, is prevented during metallization.

Semiconductors

Room 306 - Session SC+EL+SS-WeM

Passivation and Etching of Semiconductors

Moderator: Y.J. Chabal, Bell Laboratories, Lucent Technologies

8:20am **SC+EL+SS-WeM1 Infrared Study of the Initial Stages of Etching of Si Electrode Surfaces in HF Solution***, Y. Kimura, Y. Kondo, J. Nemoto, **M. Niwano**,* Tohoku University, Japan

Porous Si has been a promising class of materials used for light-emitting devices and nano-scale electronic devices, and a number of theoretical and experimental investigations have been performed on the formation and optical properties of porous Si. A conventional method of synthesizing porous Si is to apply an anodic (positive) potential to a Si electrode in aqueous etching solutions such as dilute hydrofluoric acid (HF) solution. However, the mechanism of pore formation has not been fully understood. In order to control the structure of porous Si, we need an understanding of the microscopic etching process of Si electrode surfaces during immersion in etching solution. In this study, we have investigated in-situ and in real time the etching process on p-Si(100), (111), and (110) electrode surfaces in dilute HF solution, using infrared absorption spectroscopy (IRAS) in the multiple internal reflection (MIR) geometry, and analyzed infrared absorption spectra in the Si-H stretching vibration region of the electrode surface to examine how surface Si atoms are removed. At electrode potential below approximately 1 V, surface roughening occurs to produce hydride species in the vicinity of the electrode surface. At initial stages of etching of a Si(100) electrode, monohydride species is dominantly populated by the removal of dihydride species on the topmost layer of the electrode surface. We suggest that removal of monohydride species is favored over that of dihydride species, leading to the formation of pores on the etched surface. At electrode potential above 1 V, all the hydride species are etched away, leading to electropolishing of the surface. For electrochemical etching of Si(110), monohydride species are removed from the topmost layer to populate dihydride species on the second layer of the surface. For etching of the Si(111) surface, it appears that removal of surface Si atoms more favorably takes place at step sites than on terraces.

8:40am **SC+EL+SS-WeM2 Electrical Transport at Chemically Modified Silicon Surfaces***, O. Hul'ko, R. Boukherroub, C. Mark, S.N. Patitsas, H.Z. Yu, **G.P. Lopinski**,* National Research Council Canada

We are exploring methods for tailoring the electrical conductivity of silicon surfaces via the covalent attachment of atomic and molecular adsorbates. A method for studying the electrical transport properties of wet-chemically modified silicon surfaces has been developed and applied to study of chlorine terminated Si(111). Resistivity measurements (4-probe, van der Pauw geometry) were performed on low doped n-type Si (111) substrates patterned with titanium silicide contacts. These contacts were found to withstand the RCA clean and ammonium flouride etching procedures required to prepare the atomically flat, highly ordered hydrogen terminated Si(111) surfaces that are the starting point for fabricating chemically modified Si(111) surfaces. Chlorine-termination was achieved by UV irradiation of H/Si(111). The resulting surfaces were characterized by STM and Auger, indicating a monolayer of Cl in an ordered (1x1) structure. These Cl/Si(111) surfaces showed a significant (at least one order of magnitude) increase in conductivity with respect to H/Si(111). Under ambient conditions the conductivity decreased exponentially with a time constant of ~1hr., eventually returning to the value measured before chlorination. The enhanced conductivity of the Cl/Si(111) surface is attributed to increased carrier density in the near surface region due to upward band banding caused by the electron withdrawing nature of the adsorbed chlorine. In order to explain the increased conductivity this band bending must be sufficient to cause inversion (>0.6eV). Capacitance measurements indicate that the near surface carrier concentration is increased by at least a factor of 1000 upon chlorination, consistent with the observed conductivity change. Results on other chemically modified surfaces will also be presented.

9:00am **SC+EL+SS-WeM3 Using Micromachined Test Patterns to Study Surface Chemistry: An Investigation of Etchant Anisotrophy***, **M.A. Hines**, R.A. Wind,* Cornell University

We have developed a new technique for the rapid quantification of etchant anisotropy (i.e. orientation-dependent etch rates), which uses micromachined test patterns. Although macroscopic anisotropy cannot be inverted to provide detailed atomic mechanisms, macroscopic anisotropies do provide important clues to the underlying chemical reactions. For example, an etchant that produces atomically flat silicon surfaces -- a "perfect" etchant -- must selectively etch all defect sites, while leaving the flat surface virtually untouched. Macroscopically, this implies that a perfect etchant must attack vicinal surfaces much more rapidly than flat surfaces. Our standard test pattern consists of 180 1°-wide wedges arranged in an evenly spaced, circular array. Each wedge is bounded by a different set of vertical planes, so the sides of each wedge etch with a characteristic, face-dependent rate. Anisotropic etching leads to the development of a "flower pattern," which can be analyzed to yield absolute, face-spec ific etch rates of 180 surfaces simultaneously. Etch rates measured with this technique are in good agreement with those previously reported in the literature. This technique opens to door to a pseudo-combinatorial approach to etchant development. For qu a ntitative interpretation of these data, we constructed a simple model of orientation-dependent etching that is based on step-flow etching. We tested this model on a number of different anisotropic etchants, and the model performed surprisingly well. Interestingly, there was no evidence of direct step-step interactions or step coalescence on vicinal Si(111) surfaces during etching (within approx. 20° of the close-packed plane).

9:20am **SC+EL+SS-WeM4 Etching of BPSG Films Using Anhydrous HF**, *A. Thorsness, G. Montano,* ***A. Muscat,*** University of Arizona

The absorption of water within BPSG films and its affect on the rate and the product distribution on the surface during etching with anhydrous HF (AHF) has been studied with transmission FTIR and ellipsometry. Gas phase HF chemistries are currently used to selectively etch doped oxide films relative to undoped films for both DRAM and MEMs applications, but often require a post-process water rinse. BPSG films containing 3.5%B/4.0%P were deposited to a nominal thickness of 5K Å on 8" Si wafers containing a 2K Å TEOS buffer layer. Sets of 25 wafers were annealed after deposition to four different temperatures: as deposited (400°C), 500°C, 750°C, and 900°C. The films were etched at atmospheric pressure and at temperatures from 25 to 75°C in a commercial gas phase oxide etching tool (FSI Excalibur ISR) using AHF in a nitrogen carrier. Water uptake by the films did not saturate but increased at a steady rate as a function of annealing temperature during storage in a cleanroom. Absorbed water reacted with P=O producing P-OH groups. The induction time to start etching decreased with water absorption and loss of P=O. Based on relative bond strengths AHF attacks the P-O bonds first opening up the silicon dioxide lattice and producing both a P-bearing acid and product water. The product water H-bonds to the P-bearing acid creating a thin liquid film on the wafer surface. The liquid film supports etching of the stronger Si-O-Si and B-O-Si bonds and solvates etching products. The water H-bonded to the P-bearing acid lowers the activation barrier to breaking Si-O bonds by forming a (SiO)HOH complex. The weakened Si-O bond is more amenable to attack by a polar HF molecule. Metaphosphoric acid, pyrophosphoric acid, boric acid, boron trifluoride, and water were present in the liquid films after etching. The relative amount of these products was a strong function of the annealing temperature.

9:40am **SC+EL+SS-WeM5 Etching of Polymer-like a-Si:H Films by Impact of H**, ***T. Zecho,*** *B. Brandner,* Universitaet Bayreuth, Germany*; J. Biener, J. Kueppers,* Max-Planck-Institut fuer Plasmaphysik (EURATOM Association), Germany

Etching of a-Si:H thin films with H atoms is a well known phenomenon from earlier studies. Nevertheless, the product distribution and the temperature dependence of the absolute etching rate could not be unambiguously determined. The present study was performed in order to quantify the etching rate by direct detection of the etching products during H admission and to determine to what extent higher silane species contribute to the etching process. A-Si:H films in a thickness range ca 1 to 100 nm were deposited at 300 K by ion-beam-deposition on a Pt(111) substrate and characterised by AES, TPD, HREELS and ELS. The films grow in a two-dimensional fashion and show a polymer like structure with a hydrogen content of about 40 %. The thermal stability of the films is limited by the formation of a Pt silicide commencing ab about 500 K which proceeds at the a-Si:H/Pt interface. In accordance with the exothermic formation of volatile silanes a constant etching rate of about 1 % between 100 K and 300 K was found with about equal contributions from the silane and higher silanes channels. In this temperature range even minor impurities lead to a decrease of the etching rate. From 300 K to 500 K the etching rate decreased roughly linear to 0.1 % due to the growing thermal instability of the higher silanes. Therefore at 500 K silane was the only detected etching product. The formation of both silane and higher silanes proceeds via a direct interaction of atomic hydrogen and the corresponding precursor species.

10:00am **SC+EL+SS-WeM6 Reaction Mechanism of Si(100) Etching by Mass- and Energy-Selected Cl+ Beams**, ***S.M. Lee,*** *M. Lu, J.W. Rabalais,* University of Houston

Plasma etching of semiconductor materials is a standard manufacturing technique used in integrated semiconductor industries. Due to the high operational pressures used in this process, it is difficult to study the basic etching mechanism. While plasma etching is a dynamic process, many studies have been done on the more static systems using analysis techniques like temperature programmed desorption (TPD). In this work, the kinetic energy and temperature dependencies of Cl+ beam etching of Si (100) have been studied by Auger electron spectroscopy (AES), X-ray photoelectron spectroscopy (XPS), reflection high energy electron deflection (RHEED), and positive and negative energy-filtered secondary ion detection. Ion kinetic energies were varied over the hyperthermal range of 1 - 500 eV and sample temperatures were varied over the 25 - 700Â° C range. Chemical etching dominates in the low energy range, while both chemical and physical etching processes are prevalent at the higher energies. Both the AES and XPS results demonstrate that the amount of Cl deposited on the surface is a strong function of the ion energy. The RHEED study of the surface crystallinity clearly showed the existence of synergetic effects due to simultaneous ion bombardment and annealing. A nearly ideal (2x1) surface reconstruction was obtained under the conditions of 100 eV Cl+ etching at 600Â°C. AES analysis demonstrated that the main source of surface disordering at lower temperatures and lower kinetic energies is residual Cl in the surface region. The etching products, the kinetic energy distribution of each species, and the critical kinetic energy for the etching process have been measured for different temperatures by using the positive and negative ion detector. The overall reaction mechanism is discussed based on the results obtained.

10:20am **SC+EL+SS-WeM7 Deuterium Etching of the Si-rich SiC(0001)-(3x3) Surface Reconstruction**, ***C.R. Stoldt,*** *C. Carraro, R. Maboudian,* University of California, Berkeley

The low-energy electron (LEED) pattern of the SiC(0001)-(3x3) surface reconstruction undergoes a conversion from (3x3) to (1x1) upon exposure to atomic hydrogen (and deuterium). Using high-resolution electron energy loss spectroscopy, Auger electron spectroscopy, LEED, and temperature programmed desorption, we have determined that this conversion is due to etching and disordering of the uppermost Si layers. With increasing deuterium exposure at 320 K, etching results in depletion of the Si adlayer and formation of SiD surface species. At high deuterium exposure, observation of the C-D stretch mode indicates the onset of bulk silicon carbide etching. SiD@sub 2@ and SiD@sub 3@ surface species, known intermediates in the Si etching process, are observed with deuterium exposure at 180 K.

10:40am **SC+EL+SS-WeM8 Variable Temperature Study of Hydrogen and Deuterium Passivation of the Si(100)-2x1 Surface using the Scanning Tunneling Microscope**, *M.C. Hersam,* ***N.P. Guisinger,*** *K. Cheng, J. Lee, J.W. Lyding,* University of Illinois

Deuteration of dangling bonds at the Si/SiO@sub 2@ interface has led to a significant reduction of hot carrier degradation in complementary metal-oxide-semiconductor (CMOS) circuits. Although CMOS transistors are annealed in a D@sub 2@ environment, the presence of H in the oxide leads to the interface being unavoidably exposed to both H and D during the passivation process. Thus, an understanding of the parameters that affect the equilibrium quantities of H and D on Si surfaces is of notable interest. In this paper, the relative concentrations of H and D on the Si(100)-2x1 surface are studied following in situ passivation under conditions of equal H and D pressure. Electron stimulated desorption with a scanning tunneling microscope allows for atomically precise determination of the H and D levels. The ratio of D to H on the Si(100) surface is measured to be ~50 and ~5 following monolayer passivation at 350 K and 650 K respectively. This behavior can be qualitatively understood through a statistical thermodynamics model. Ultimately, the magnitude of the D:H ratio and its inverse relationship with passivation temperature result from the difference in the vibrational frequencies for Si-H and Si-D bonds. These results imply that the optimal deuteration of silicon dangling bonds in the presence of background H should occur at low sample temperatures. Since CMOS processes are continually reducing their thermal budgets to accommodate additional metal layers and novel materials (e.g., low k dielectrics), this paper fundamentally suggests that deuteration of the Si/SiO@sub 2@ interface could improve as processing temperatures are inevitably lowered in the future.

Surface Science
Room 208 - Session SS1-WeM
Chemical Interactions and Surface Reactivity

Moderator: J.L. Gland, University of Michigan

8:20am **SS1-WeM1 Increased Reactivity of Strained Ni Layers on Ru(0001)**, ***R.C. Egeberg***, *I. Chorkendorff,* Technical University of Denmark, Denmark

Understanding the reactivity of metal surfaces and in particular how to control and manipulate this reactivity is the first step towards improved catalysts. From many surface science studies a detailed knowledge about the structures emerging from metal on metal growth has been gained whilst the link to the overall reactivity of such bimetallic structures has not been equally thoroughly investigated. We here present data showing how to utilize the growth properties of Ni on Ru(0001) to improve the ability of Ni to catalyze the reforming of methane. By growing a pseudomorphical Ni overlayer on Ru(0001) a strained Ni layer is formed with respect to Ni(111). As a result of the change in electronic configuration this procedure results in a more reactive Ni layer as it has been predicted from DFT calculations. In steam reforming catalysis the dissociation of methane is the rate-limiting step and we have therefore focused on the initial sticking of methane on this surface. Thermal experiments at 530 K show that the Ni overlayer is ca. 2 times more reactive than Ru(0001) and ca. 20 times more reactive than Ni(111). As more than 1 monolayer of Ni is deposited the sticking decreases and saturates at the value for Ni(111). The adsorption energy of CO which is used as a probe molecule follows the same trend as the CH@sub 4@ sticking. Supersonic molecular beam experiments support the picture of a lower activation barrier on the strained Ni overlayer. Finally, the ability of the surface to catalyze the partial oxidation of methane is under investigation.

8:40am **SS1-WeM2 Suppression of NO Dissociation by Adsorbed Gold on Pt(335)**, ***D.C. Skelton,*** Michigan State University / General Motors*; R.G. Tobin,* Tufts University*; C.L. DiMaggio, D.K. Lambert, G.B. Fisher,* Delphi Automotive Research Labs

We have conducted a temperature programmed desorption study to compare the dissociation probabilities of oxygen and NO on a partially gold-covered stepped Pt(335) surface. NO dissociation takes place almost exclusively at step sites. It apparently requires either multiple adjacent open step sites, or special sites such as kinks, and is therefore unusually sensitive to modification of steps and defects. A gold coverage of 0.15 ML reduces NO dissociation by a factor of five compared to bare Pt, and increasing the gold coverage to 0.3 ML further reduces it to an undetectable level. Oxygen dissociation also occurs preferentially at step sites, but is far less sensitive to step blockage: At 0.3 ML gold, the saturation oxygen coverage is only 20% lower than on bare Pt. These results help explain the operation of a recently developed electrochemical NO@sub x@ sensor.@footnote 1@ An effective NO@sub x@ sensor is vital for pollution control in fuel-efficient lean-burn gasoline and diesel engines. The electrochemical sensor uses a platinum-gold alloy electrode in a pumping cell to remove oxygen from the exhaust gas without dissociating NO. For effective sensor operation, the electrode must be ~10@super 3@ more effective at dissociating oxygen than at dissociating NO. Our experiments suggest that a platinum-gold alloy electrode has this remarkable selectivity because gold blocks special sites that are needed for NO dissociation but not for oxygen dissociation. @FootnoteText@ @footnote 1@ N. Kato, Y. Hamada and H. Kurachi, SAE Paper 970858 (1997).

9:00am **SS1-WeM3 Chemical and Electronic Properties of Ni/Pt(111) Bimetallic Surfaces: Unique Surface Reactivity at the Monolayer Ni Coverage**, ***J.G. Chen****, J. Eng, Jr., M.T. Buelow, H.H. Hwu, N.A. Khan,* University of Delaware **INVITED**

In a recent paper we reported the observation of an "anomalous" reactivity of Ni/Pt(111) bimetallic surfaces at Ni coverages around one monolayer (ML) [3]. For example, after a saturation exposure of D2 to a Ni/Pt(111) surface with one ML Ni, the desorption of D2 occurs at 220 K from the TPD measurements. This desorption temperature is lower than that of D2 desorption from either Pt(111) (294 K) or Ni(111) (379 K). The lower desorption temperature suggests that the D atoms are rather mobile on the one ML Ni/Pt(111) surface. We have tested this idea by investigating the hydrogenation of cyclohexene to cyclohexane, and the hydrodesulfurization of thiophene to 1,3-butadiene on the one ML Ni/Pt(111) surface. In both cases the hydrogenation reactions take place at around 220 K under UHV conditions; these two reactions do not occur on either Pt(111) or Ni(111) under similar experimental conditions. In this talk we will present these latest TPD results, as well as our characterization of the chemical and electronic properties of the Ni/Pt(111) surfaces using high-resolution electron energy loss spectroscopy (HREELS), near-edge X-ray absorption fine structure (NEXAFS), and X-ray photoelectron spectroscopy (XPS).

9:40am **SS1-WeM5 Coverage Dependent Selectivity and a New Approach to Tayloring Nanostructures on Single Crystal Surfaces**, ***A.V. Teplyakov****, H. He, A.T. Mathauser,* University of Delaware

Here we report a remarkable chemistry exhibited by 6-bromo-1-hexene on a Cu@sub 3@Pt(111) surface. The dehydrocyclization reaction leading to the formation of benzene takes place at very low coverage; as the surface fills up the decomposition becomes a predominant pathway. Similar behavior was reported for other linear hydrocarbons on metals and metal alloys previously. However, further increase of surface concentration of 6-bromo-1-hexene leads to a different type of chemistry. The hydrogenation of 5-hexenyl produced as a result of C-Br bond dissociation leads to the formation of 1-hexene which is stable on a surface until the molecular desorption of this compound starts at 230 K. Molecular desorption from the monolayer becomes significant at even higher dose. All these processes occur within a specific coverage very cleanly making the 6-bromo-1-hexene on a Cu@sub 3@Pt(111) surface extremely attractive to analyze the kinetics of coverage dependent processes. Steric requirements for each of the processes described here and the availability of the adsorption sites on the alloy surface are believed to govern the predominant reaction. Thermodynamics and potential applications of these chemical processes for masking and production of nanoscale features will be discussed.

10:00am **SS1-WeM6 The Near Edge X-ray Absorption Fine Structure of n-octane Adsorbed on Cu(110): New Insights Into the Type of Chemical Interaction**, ***K. Weiss****, L. Triguero, H. Öström, A. Nilsson,* Uppsala University, Sweden

Using near edge X-ray absorption fine structure (NEXAFS) spectroscopy we have investigated the electronic structure of n-octane adsorbed on Cu(110). The molecule is found to be well oriented on the surface, which is seen from the high degree of NEXAFS dichroism. The NEXAFS spectra, which display the density of unoccupied molecular states, reveal large changes in the electronic structure of the adsorbed octane relative to the free molecule. We find that the molecular Rydberg states are strongly quenched upon adsorption and that there is a significant hybridization of molecular valence orbitals with the metal bands. In order to understand these adsorption induced electronic structure changes we have performed cluster model calculations in the framework of density functional theory. The calculations show nice agreement with the experimental results. In addition to a precise interpretation of the NEXAFS spectra, we present details on the geometric structure of the adsorbed octane molecule and the molecular orbital structure. The results are complemented by calculations of the X-ray emission spectra, which provide information on the occupied valence states. Our study gives new insights into the type of chemical interaction experienced by saturated hydrocarbons adsorbed on metal surfaces, which is of importance for the understanding of the C-H bond activation mechanism.

10:20am **SS1-WeM7 Direct Experimental Measurement of Donation/Backdonation in Unsaturated Hydrocarbons Bonding to Metals**, ***L. Triguero***, Uppsala University, Sweden*; A. Föhlisch,* Universität Hamburg, Germany*; P. Väterline, J. Hasselström,* Uppsala University, Sweden*; M. Weinelt,* Universität Erlangen, Germany*; L.G.M. Pettersson,* Stockholm University, Sweden*; A. Nilsson,* Uppsala University, Sweden

Soft X-ray emission spectra (XES) from C@sub 2@H@sub 4@/Cu(110) and C@sub6@H@sub6@/Cu(110) have been obtained for two excitation energies, resonant and non-resonant, and resolved in all three spatial components (x, y, z). The one-step theory for resonant soft X-ray spectroscopy and Raman scattering is extended to adsorbates on metal surfaces and is implemented within a density functional theory framework. A combination of these expermiental and theoretical works are used to examine the electronic structure of chemisorbed ethylene and benzene on the Cu(110) surface in order to investigate the suitability of the donation/backdonation bonding model given by Dewar, Chatt and Duncanson for the interaction of unsaturated hydrocarbons with metal surfaces. We give an experimental verification of the DCD model and find donation/backdonation to be twice as large for ethylene as for benzene. In particular, the degree of @sigma@--@pi@ mixing (rehybridization) is found to correspond to the amount of donation/backdonation, which is put into relation to the aromatic and non-aromatic @pi@ characters of benzene and ethylene, respectively.

10:40am **SS1-WeM8 Trapping-mediated Dissociative Chemisorption of Cycloalkanes on Ru(001) and Ir(111): The Influence of Ring Strain on the Activation of C-C and C-H Bonds***, **T.-W. Kim**, C.J. Hagedorn, M.J. Weiss, W.H. Weinberg,* University of California, Santa Barbara

We have measured the initial probabilities of dissociative chemisorption of perhydrido and perdeutero cycloalkane isotopomers on the hexagonally close-packed (hcp) Ru(001) and Ir(111) single-crystalline surfaces for surface temperatures between 250 and 1100 K. Kinetic parameters (activation barrier and preexponential factor) describing the initial, rate-limiting C-H or C-C bond cleavage reactions were quantified for each cycloalkane isotopomer on each surface. Determination of the dominant initial reaction mechanism as either initial C-C or C-H bond cleavage was judged by the presence or absence of a kinetic isotope effect between the activation barriers for each cycloalkane isotopomer pair, and also by comparison with other relevant alkane activation barriers. On the Ir(111) surface, the dissociative chemisorption of cyclobutane, cyclopentane, and cyclohexane occurs via two different initial reaction pathways: initial C-C bond cleavage dominates on Ir(111) at high temperatures (T > 600 K), while at low temperature (T < ~400 K), initial C-H bond cleavage dominates. On the Ru(001) surface, dissociative chemisorption of cyclopentane occurs via initial C-C bond cleavage over the entire temperature range studied, whereas dissociative chemisorption of both cyclohexane and cyclooctane occurs via initial C-H bond cleavage. Comparison of the cycloalkane C-C bond activation barriers measured here with those reported previously in the literature, suggests that the difference in ring strain energies between the initial state and transition state for ring-opening C-C bond cleavage effectively lowers or raises the activation barrier for dissociative chemisorption via C-C bond cleavage depending on whether the transition state is less or more strained than the initial state. Moreover, steric arguments and metal-carbon bond strength arguments have been invoked to explain the observed trend of decreasing C-H bond activation barrier with decreasing cycloalkane ring size.

Surface Science
Room 209 - Session SS2-WeM
Stimulated Surface Processes

Moderator: R.M. Osgood, Columbia University

8:20am **SS2-WeM1 Enhanced Adatom Diffusion Using Glancing-Angle Ions***, S.A. Barnett, **K.C. Ruthe**,* Northwestern University*; P.M. DeLuca,* Kopin

We describe the effects of glancing incidence (3°) 3-4 keV Ar ion bombardment on homoepitaxial growth on vicinal GaAs (001). The average adatom lifetime on surface terraces was measured during GaAs deposition using specular ion scattering. The lifetime was observed to decrease monotonically with increasing ion current density, e.g. from 1.8 to 0.8 s for a current density increased from 0.6 to 22 mA/cm2 at a temperature of 520C (GaAs miscut = 2.5). There was no measurable sputtering, and the results suggested that the Ga surface diffusivity was increased by the ions. The ion beam also suppressed scattered ion beam current oscillations, suggesting that the growth mode had changed from two-dimensional island nucleation to step-flow due to increased adatom surface diffusivity. The RMS roughness of 0.3 micron thick GaAs epitaxial layers, measured by atomic-force microscopy, showed a corresponding decrease from 0.5 to 0.25 nm due to ion bombardment. A simple model, involving direct momentum transfer from ions to adatoms parallel to the surface, is shown to be consistent with the measured diffusion enhancements.

8:40am **SS2-WeM2 Scattering of Hyperthermal O@super +@ Ions on a SiO@sub x@ Surface***, **C.L. Quinteros**, T. Tzvetkov, D.C. Jacobs,* University of Notre Dame

Thin SiO@sub x@ films are grown on a Si(100) surface using a low current, hyperthermal (5-200eV) O@super +@ beam under UHV conditions. Scattered products are collected as a function of incident beam energy and angle, oxygen ion dose, temperature, and surface roughness. A rotatable quadrupole mass spectrometer detector resolves the energy-, mass-, and angular-distributions of the scattered species. Incident O@super +@ is efficiently neutralized, and both positively (Si@super +@, SiO@super +@) and negatively (O@super -@, O@sub 2@@super -@) charged products are formed. The product ion yields strongly increase with O@super +@ dose, as the oxide film develops. Individual features in the energy distributions of the scattered products are assigned to scattering events occurring at particular atomic sites on the surface. Product channel contributions originating from chemical reaction with incident O@super +@ and physical sputtering are differentiated.

9:00am **SS2-WeM3 Film Growth and Surface Modification by Low Energy Polyatomic Ions***, **L. Hanley**,* University of Illinois at Chicago **INVITED**

Polyatomic ions with collision energies from 5 - 200 eV can be used to deposit films and modify surfaces in a highly controllable fashion. Low energy polyatomic ions are very surface selective, interact with surfaces via a unique collision dynamics, and can be used to transfer part or all of their chemical functionality to a surface. Ionization and mass-selection permits the facile preparation of a wide range of reactive species. Collision energy can be further used to control the final film properties. Examples discussed will include the deposition of 1) cross-linked fluorocarbon films on polystyrene by 25 - 100 eV CF@sub 3@@super +@ and C@sub 3@F@sub 5@@super +@ and 2) cross-linked organosiloxane films on Al by 15 - 100 eV Si@sub 2@O(CH@sub 3@)@sub 5@@super +@. Monochromatic x-ray photoelectron spectroscopy and contact angle measurements are used to determine film chemistry. Atomic force microscopy and x-ray reflectivity are used to determine film thickness and morphology. Oxidation and other aging processes are also examined for these films following air exposure for several weeks. Molecular dynamics simulations support the experimental results and compare the surface interaction process for different ion isomers. These results show that the size and structure of the depositing ion affects film formation via different chemical structure, reactivity, sticking probabilities, and energy transfer to the surface. These results also indicate that polyatomic ions and energetic neutrals likely play an important role in film deposition and surface modification during plasma polymerization, laser ablation of polymers, and sputter deposition of polymers.

9:40am **SS2-WeM5 Super-smooth Neutron Optical Surfaces By Gas Cluster Ion Beam Processing***, L. Stelmack,* Epion Corporation and Northeastern University*; **L.P. Allen**,* Epion Corporation*; V. DiFilippo,* Epion Corporation and Tufts University*; J.A. Greer, D.B. Fenner, R. Chandonnet, J. Hautula, A. Kirkpatrick,* Epion Corporation

The neutron scattering research community has continuing need for advancing the technology required to produce improved neutron optical components, particularly in regard to increasing efficiency and reducing non-specular scattering from substrate surfaces and coating interfaces. A novel Ar gas cluster ion beam (GCIB) process was implemented in order to determine the effectiveness of the extreme GCIB surface smoothing technique as it applies to improving neutron optical component substrates and coatings. A matrix of GCIB smoothing conditions was applied on selected optical structures. Pre- and post-GCIB processed surfaces of Si, SiO2, Ni/Si, Ta, and Ni/Ta/ SiO2/Si substrates were examined with atomic force microscopy for surface roughness and overall film morphology. Silicon substrate surfaces coated with Ni were found to be consistently smooth to Ra ~1Å. In addition, results show that the Ni and Ta coated surfaces consistently achieved smoothness capable of supporting optical requirements for advanced neutron sources. The GCIB process parameters as applied to optical (SiO2, Ni/S, Al2O3), semiconductor (Si), and metallic (Cu, Ta, Ti, Ni) surfaces are shown to provide a predictable surface smoothness (Ra typically <3Å) for applications in a variety of material related fields.

10:00am **SS2-WeM6 Molecular Dynamics Simulation of Hyperthermal Ne@super +@ Scattering From Si(100)***, J. Camden, **T. Tzvetkov**, C.L. Quinteros, D.C. Jacobs,* University of Notre Dame

An understanding of ion/surface energy transfer at hyperthermal energies is important to the semiconductor industry, where low-energy ion modification of surfaces is widely employed. In this paper, we present molecular dynamics simulations of Ne@super +@ scattering from Si(100) at hyperthermal energies (below 200eV). In the trajectory calculations, we use a Ne-Si potential consisting of pair-wise additive terms describing the repulsion between the projectile and all Si atoms within a slab, and a classical image charge attraction between Ne@super +@ and the bulk dielectric. The surface reconstruction is taken into account in the Si lattice simulation. A careful analysis of different trajectory contributions to the scattering signal is applied. The calculations for different surface conditions, including scattering from surface defects (steps, adatoms and vacancies), will be discussed. The calculations are compared to experimental results for Ne@super +@ scattering from Si(100) at energies ranging from 25 to 200 eV.

10:20am **SS2-WeM7 Laser Induced Reactivity of Ammonia on Silicon Surface*, T. Gonthiez,*** *P. Brault,* GREMI (University of Orleans-CNRS), France*; T. Gibert,* GREMI (University of Orleans), France

In the field of the growth of materials like Si@sub3@N@sub4@ or AlN, photochemical processes are of a great interest. A study of the reactivity of surface induced by laser of NH@sub3@ on Si(100) is undertaken. Laser fluence and NH@sub3@ pressure are low enough just to realize the first steps of the process. Experimental studies are performed in an ultra-high vacuum chamber. Gaz is introduce by a µ-leakage valve near the surface. A UV laser beam (266/355 nm) is used to activate reactions at gaz-surface interface or to desorb the surface for analysis. Due to initial surface contamination, reactions between NH@sub3@ and Si are self-limiting. Indeed O and C contaminant atoms tie up the surface dangling bonds leading to a passivation layer.@footnote1@ By Auger Electron Spectroscopy, we find that laser irradiation on Si cleans the surface and regenerates the dangling bonds. Analysis of the desorbed species during or after the reaction provides information on reactions at surface. The flying ionic species are directly detected by a quadrupolar mass spectrometer and the neutrals are postionized by a tunable laser. The resonant or non-resonant post-ionization techniques are useful to measure Time-of-Flight distribution of flying species by adjusting the delay between desorption and probe laser. TOF distributions can be fitted by suitable velocity distribution and this allows the determination of kinetic temperature.@footnote2@ This temperature has been shown to be the surface temperature during the laser interaction. Direct measurements of flying ions show several species and mainly Si@sub2@N, Si@sub2@NH, Si@sub2@NH@sub2@ and Si@sub2@NH@sub3@. Comparison between silicon TOF signal with and without NH@sub3@ is expected to give more insight in the nitride bond formation. @FootnoteText@ @footnote 1@Ph.Avouris, F.Bozso, RJ Hamers - J.Vac.Sci.Techno.B 5(5), Sept/Oct 1987; 1387-1392 @footnote 2@ T.Gibert, B.Dubreuil, MF.Barthe, JL Debrun-J.Appl.Phys 74, 3506 (1993).

10:40am **SS2-WeM8 Interaction of Laser Impulse with YBA@sub2@CU@sub3@O@sub7@ Target and Generation of Four Element Plasma*, I.Yu. Davletov,*** Urganch State University, Uzbekistan*; M.R. Bedilov, R.M. Bedilov,* Tashkent State University, Uzbekistan

In this work the results of studies of interactions of laser radiation with HTSC-targets are presented. The experiments have been performed by using a laser mass-spectrometer and HTSC-materials in the from of tablets of 1,0 cm diameter and thickness 0,5 cm. It was established experimentally that along with heating, destroying and evaporation of the target under interaction of the laser radiation at q>10@super9@ W/cm@super2@ with HTSC-targets, the four element plasma has been formed. Mass, charge, velocity, time and energy spectra of ions emitted from HTSC-target were studied in a wide range of the laser power. It was revealed that mass-spectra of HTSC-target atom ionized by the laser radiation contained not only one-charged ion peaks of basic element of the target but also signals of multiply charged atoms of the elements. The experiment showed, that ions with Z>1 are emitted from the HTSC-target by one-electron mechanisms of ionization of the four-element target by the laser radiation in the range of 10@super8@ W/cm@super2@ - 10@super11@ W/cm@super2@ (branch feature). Note that the formation of target ions Y@super+1@ , Cu@super+1@, Ba@super+1@, O@super+1@ begins at the power density of the laser radiation q@super8@ W/cm@super2@, and Cu@super+2@, Y@super+2@ at q@super2@ W/cm@super2@. The charge and energy distributions of the multicharged ions of the HTSC-target are determined by processes of triple recombination and energy exchange of non. Coulombic collisions between them. The energety spectra of the HTSC-target ions are analogous to those of a mono-element target, but the decreasing of the maximal energy of the ions of each multiplicity resulted from energetic losses due to Coulombic collections. The influence of oxygen state in the HTSC-target is established.

Surface Science
Room 210 - Session SS3-WeM
Gas/Surface Dynamics

Moderator: B.D. Kay, Pacific Northwest National Laboratory

8:20am **SS3-WeM1 Rainbow Scattering of Methane and Ethane Molecular Beams from a LiF(001) Surface: Dependencies on Incident Kinetic Energy and Molecular Anisotropy*, T. Kondo*,** *T. Tomii, S. Yamamoto,* University of Tsukuba, Japan

An experiment to measure the angular distribution of the intensity of the alkane molecular beams scattered from a highly corrugated surface of LiF(001) has been carried out in high resolution, as a step toward the understanding of the fundamental characteristics of surface chemical reactions. One of the two major findings of the experiment shows that the rainbow peaks of the molecular beam was found to depend on its incident kinetic energy. For the clarification of this dependency, we calculated the angular distribution applying the Washboard model@footnote 1@ to fit the results by changing the amplitude of the sinusoidal corrugation in each case of different incident kinetic energy, instead of fixing the amplitude once fitted for the lowest incident kinetic energy. In this way it was further confirmed that the intensity of the rainbow peaks was reduced as the incident kinetic energy increases, contrary to the result predicted with the fixed amplitude. The reason for this discrepancy is thus because the combined structure of Li and F ions weakens the corrugation of the potential energy surface for the beam with increased incident kinetic energy. As the other major finding, the ethane molecular beam shows only one peak but not the rainbow peaks, in spite of negligible difference in the molecular size between the methane and the ethane molecules. On the other hand, the Ar atom which is heavier than both the above alkane molecules shows the distinct rainbow peaks. It is then presumed that the effect of neither the size nor the mass of the molecule is essential for the rainbow peaks. Therefore, the difference in behavior between the methane and the ethane molecules can be understood as a result of the large anisotropy of the ethane molecule. @FootnoteText@ @footnote 1@J. C. Tully. J. Chem. Phys. 92, 680 (1990).

8:40am **SS3-WeM2 Probing the Extrinsic Precursor State: Methane Trapping on Ethylidyne-covered Pt(111)*, A. Carlsson*[1]*,*** *R.J. Madix,* Stanford University

Under steady state conditions in catalytic reactions surfaces may be covered with stable species that affect the adsorption kinetics. It has been well documented that the adsorption probability of many molecules is facilitated by a species which can migrate across the adsorbed layer in search of a binding site. This species is referred to as an extrinsic precursor state. In order to obtain a more general understanding of this precursor state and its effect on adsorption, we have studied the kinetics of methane trapping on ethylidyne-covered Pt(111) with supersonic molecular beam techniques at surface temperatures spanning the range in which methane desorbs from the saturated monolayer and the second adsorbed layer. Because the surface is nearly saturated with ethylidyne, in order to adsorb methane must first occupy an extrinsic precursor state and then migrate to vacant sites within the ethylidyne structure to adsorb. In accordance with a precursor model for adsorption, the dependence of the adsorption probability on surface temperature gives the difference in activation energies for desorption and migration from the extrinsic precursor and the ratio of pre-exponential factors. The temperature dependence of the steady state coverage was used to determine the activation energy for conversion of the adsorbed state back into the extrinsic precursor to be 5.7 kJ/mol, compared to the desorption energy from the extrinsic precursor of about 9 kJ/mol.

9:00am **SS3-WeM3 Gas-Surface Dynamics of State-Selected Reagents*, A.L. Utz*,** *L.B.F. Juurlink, R.R. Smith, C.L. DiCologero,* Tufts University **INVITED**

We use supersonic molecular beams of rovibrationally state-selected molecules to probe methane dissociation dynamics on Ni(100). These studies reveal key features of the gas-surface potential energy surface governing activated dissociative chemisorption. Excitation of the @nu@@sub 3@ antisymmetric C-H stretching vibration enhances reactivity by a factor of 1600 relative to molecules in v=0, which points to the important role of C-H stretch excitation in methane activation. The Coriolis-coupled sublevels of the triply degenerate @nu@@sub 3@ mode differ considerably in the relative motion of the four excited C-H oscillators, but they share a similar efficacy for promoting dissociation. This

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

observation suggests that the reactivity of @nu@@sub 3@ is likely derived from its C-H stretching character in the one C-H bond that is properly oriented for dissociative chemisorption, but not from the collective motion of all four C-H oscillators in the molecule. Rotational-state-resolved studies show that @nu@@sub 3@ reactivity varies by less than a factor of two from J=0 to 3 and provide tentative support for dynamical steering effects. Studies of other vibrational states in methane provide a dramatic example of vibrational mode specificity in a gas-surface reaction. We find that the second overtone of the @nu@@sub 4@ triply degenerate bending mode, 3@nu@@sub 4@, is at least five times less reactive than @nu@@sub 3@, despite its containing 30% more internal energy. Mode specificity establishes that a vibrationally excited molecule retains enough memory of its initial state to influence its reactivity on a metal surface. The lack of reactivity in the @nu@@sub 4@ coordinate, coupled with the absolute reactivities we measure for the @nu@@sub 3@ state, suggests that combination vibrations containing both stretch and bend excitation may be the most reactive vibrational states in a thermal sample of methane.

9:40am **SS3-WeM5 Sticking Probability Measurement of Oriented NO on Al(111)***, **A.J. Komrowski,*** University of California, San Diego*; B. Berenbak,* FOM Institute AMOLF, The Netherlands*; S. Stolte,* Vrije Universiteit Amsterdam, The Netherlands*; A.W. Kleyn,* Leiden University, The Netherlands*; A.C. Kummel,* University of California, San Diego

We report that by controlling the reactant orientation immediately prior to the interaction, we have gained new insight into the dissociative and abstractive chemisorption of NO interacting with a reactive metal surface, Al(111). In a novel experiment, we have used the beam reflectivity technique to measure the sticking probability of an oriented molecular beam as a function of incident molecular orientation and translational energy. We observe a higher sticking probability when the N-end is preferentially directed towards the Al(111) surface. The difference in sticking probabilities between N-end first and O-end first interactions increases with increasing incident translational energy. In contrast, Auger spectroscopy results from non-oriented molecular beams of NO with similar energies show initial surface coverage Nitrogen/ Oxygen ratios less than unity. The results are consistent with a two step chemisorption process for the initial reaction with the clean surface. First, an electron harpoons from the metal to the N-end of the molecule. The NO@super -@ molecular ion is attracted to the surface by its image charge. Second, the molecule may absorb another electron from the surface before the intramolecular bond breaks and Oxygen is deposited onto the surface while Nitrogen is ejected into the gas phase.

10:00am **SS3-WeM6 Speed Distribution of Ethane Molecular Beam Reflected after Temporary Trapping on a LiF(001) Surface***, **T. Tomii,** T. Kondo, S. Yagyu, S. Yamamoto,* University of Tsukuba, Japan

We have measured at various scattering angles the time-of-flight of ethane molecules scattered from a LiF(001) surface of room temperature. With a high resolution cross-correlation time-of-flight technique we have successfully separated out the component of ethane molecules scattered after experiencing a temporary trapping on the sample surface. While the major peak in the time-of-flight spectrum, which consists of rotationally excited ethane molecules after single collision, can be fairly well fitted to a shifted Maxwell-Boltzmann speed distribution function, it was found that the temporarily trapped component can be reproduced by a single Maxwellian speed distribution function with a characteristic temperature lying slightly higher than the target surface temperature. This temperature tends to increase from around 300 to 600 K with the translational energy of the incident ethane beam in the range between 260 and 700 meV. The mean translational energy of the temporarily trapped molecules is almost uniform in the scattering angle, exhibiting a strong contrast to that of the directly scattered which qualitatively follows the washboard model predictions with the appropriate parameters. Despite the strong anisotropy of the ethane molecule, the directly scattered component shows a little surface rainbow features in the angular mean translational energy distribution, revealing the corrugation of the gas-surface repulsive potential. Temporarily trapped molecules are believed to be the ones which at first couple of bounces have stored their incident translational energy in the form of rotation, either cartwheel or helicopter mode, and tangential motion on a corrugated LiF(001) surface, resulting in a Maxwell-like speed distribution as a whole.

10:20am **SS3-WeM7 Trapping Dynamics of Ethane on Si(100)-(2x1) Studied by Molecular Beam Experiments and Classical Molecular Dynamics Simulations***, **C.T. Reeves**, C.B. Mullins,* University of Texas at Austin

In order to gain insight into the dynamics of trapping, or physical adsorption, we have experimentally measured the trapping probability of ethane on a clean Si(100) surface as a function of the incident translational energy and incident polar angle of the molecule at a surface temperature of 65 K using UHV molecular beam techniques. At all incident angles the trapping probability decreases as the translational energy of the incoming ethane molecule is increased from 0.05 to 1.3 eV. As the incident polar angle, with respect to the surface normal, is increased, the trapping probability decreases. This decrease in trapping probability with increasing polar angle contradicts the idea of normal energy scaling and has been seen in very few cases. Classical molecular dynamics calculations have been employed to study the cause of this unusual angular dependence. This simulation predicts trapping probabilities in good agreement with the experimental data. Analysis of the computed trajectories indicates that the initial site of impact within the unit cell, as well as the details of energy exchange during the initial impact with the surface, is important in determining the fate of an incident molecule. Although it is difficult to experimentally measure the effect of rotational energy and surface temperature on trapping, molecular dynamics simulations offer a means to study the details of these effects. Recent experimental studies by Vattuone et al. have indicated that for trapping of ethylene on Ag(001), increasing the average rotational energy from J = 2 to J = 8 can greatly decrease the trapping probability. Our simulations of ethane trapping on Si(100) have indicated that the trapping probability does decrease with increasing J, although the effect is only significant at very high values of J (>20). We have also computationally investigated the effect of surface temperature on trapping and these results will be reported.

10:40am **SS3-WeM8 Dynamics of Atom Abstraction in the Scattering of NH@sub 3@@super +@ on Deuterated Al(111)***, **M. Maazouz**, P.L. Maazouz, D.C. Jacobs,* University of Notre Dame

From a fundamental point of view, hyperthermal energy ion-surface reactions represent intriguing systems of study. The gas-surface collision energy is often high enough to drive reactions (e.g. dissociative scattering, activated chemisorption, sputtering, and atom abstraction) that are typically not observed in the thermal energy regime. Atom abstraction has been observed by many groups, yet the detailed dynamics of such hyperthermal energy reactions remain elusive. The experiment reported here examines the influence of translational energy and initial vibration quanta on the reaction of NH@sub 3@@super +@ with D/Al(111). The Al(111) surface was predosed with deuterium at 120 K, and the coverage was calibrated by TPD measurements. Resonance-enhanced mult iphoton ionization (REMPI) prepares incident ammonia ions in a specific vibration state. The ions are accelerated toward the deuterium-covered Al(111) surface at normal incidence, and the products are measured with mass-, angular-, and velocity-resolution. Specifically, the yield and kinetic energy distribution of NH@sub 3@D@super +@ is measured as a function of incident translational energy (5-80 eV) and vibration quanta (n=0-10) of NH@sub 3@@super +@.

Thin Films
Room 203 - Session TF-WeM
Modeling of Thin Film Growth

Moderator: L. Hultman, Linköping University, Sweden

8:20am **TF-WeM1 Hyperthermal Ion Enhanced Deposition of Materials***, **J.W. Rabalais,*** University of Houston **INVITED**

The chemical and physical interactions of ions with surfaces in the energy range 5 eV to several keV will be described. Hyperthermal reactive ions impinging on surfaces provide a method for deposition/growth/synthesis of materials within a unique nonequilibrium UHV environment, giving rise to the technique of ion beam deposition (IBD). IBD allows independent control over parameters such as ion energy and type, ion fluence and dose, substrate temperature, and background gases. The depth of penetration/interaction of the impinging ions with the surface is determined by the ion kinetic energy. The excellent control over ion dose allows deposition of thin films, e.g. < 30 @Ao@, with sharp film-substrate interfaces. The UHV conditions in the sample chamber allow deposition onto atomically clean and well-ordered surfaces. In situ diagnostic techniques, such as reflection high energy electron diffraction (RHEED), x-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), mass spectrometry, and a microbalance allow direction characterization of the deposited/reacted layers. Examples of the use of mass- and energy-selected beams for hyperthermal surface reactions, film growth, and shallow implantation will include: Si+ ion homoepitaxy, growth SiO2 and TiSi2 films on silicon, growth of Ti and TixAlyOz films on sapphire (a-Al2O3), controlling cationic diffusion coefficients in sapphire, and interactions of chlorotitanium ions TiClx+ with graphite and silicon surfaces.

9:00am **TF-WeM3 Thin-Film Growth on Polymer Surfaces through Polyatomic Ion Deposition: Molecular Dynamics Simulations***, **Y. Ji**, S.B. Sinnott,* The University of Kentucky

Ion deposition on polymer surfaces is widely used to deposit polymer thin films or modify the mechanical properties of the polymer surface. In this work the reactions of polyatomic ions with a polystyrene surface are investigated through classical molecular dynamics simulations. The classical reactive empirical bond order potential is used.@footnote 1@ The particular ions of interest are CH@sub 3@@sup +@ and C@sub 3@H@sub 5@@sup +@ which are deposited over a range of energies from 20 to 100 eV. The chemical reactions that occur on impact are shown to depend heavily not only on the incident energy but also on the structure and size of the ion. Information about penetration depths and energy transfers are also obtained from the simulations. The results are compared to experimental data obtained for the growth of fluorocarbon thin films through the deposition of the comparable fluorocarbon species on polystyrene. There is generally good agreement between the experimental and computational results.@footnote 2@ The simulations also address the effect of incident angle on the results of ion deposition. The differences between the reactions that occur at normal incidence and at various angles are discussed. This work is supported by the National Science Foundation (CHE-9708049). @FootnoteText@ @footnote 1@.S.B. Sinnott, L. Qi, O.A. Shenderova, D.W. Brenner, in Chapter 1 of Volume IV of ADVANCES IN CLASSICAL TRAJECTORY METHODS, Molecular Dynamics of Clusters, Surfaces, Liquids, and Interfaces, Ed. W. Hase (JAI Press, Inc., Stamford, CT, 1999), pp. 1-26. @footnote 2@M.B.J. Wijesundara, L. Hanley, B. Ni and S.B. Sinnott, Proceedings of the National Academy of Science, USA 97 23-27 (2000).

9:20am **TF-WeM4 Molecular Dynamics Simulation of Ion Bombardment on Hydrogen-terminated Si(001)-(2X1) Surfaces***, **K. Satake**,* Mitsubishi Heavy Industries, Ltd., Japan*; D.B. Graves,* University of California, Berkeley

In crystalline Si growth using low-temperature plasma enhanced chemical vapor deposition (PECVD), it is important to clarify the role of ions in the surface reactions. We present here the interaction between an H-terminated Si(001)-(2X1) surface and normal incident SiH@sub 3@ @super +@ and H@sub 2@ @super +@ ions as a function of the incident energy (10 eV, 20 eV, and 40 eV) using molecular dynamics (MD) simulations. SiH@sub 3@ @super +@ was observed to penetrate less than 3-4 Å at 10 eV and 20 eV, increasing to about 5 Å at 40 eV. H@sub 2@ @super +@ penetrated the surface only slightly at 10 eV, but the penetration depth increased rapidly with increasing energy. At 40 eV, H@sub 2@ @super +@ was observed to penetrate up to 20 Å, or even farther. Per trajectory, SiH@sub 3@ @super +@ was observed to displace about 4 Si atoms in the lattice, an average distance of about 2-3 Å, at 40 eV. H@sub 2@ @super +@, by contrast, displaced on average, only 0.7 Si atoms per trajectory, and the displacement distance was about 1.5 Å, at 40 eV. It is suspected that ion impact creates sites which react more readily with neutral species. The generation rate of dangling bonds (DB) at the surface due to H@sub 2@ @super +@ ion impact is about twice that of SiH@sub 3@ @super +@ ions for the energies studied. In the DB generation by H@sub 2@ @super +@ ions, the primary process is direct surface H atom sputtering. In addition, we also observed the DB generation with dihydride and monohydride formation by H insertion into the Si dimer and H exchange. In the case of SiH@sub 3@ @super +@ ions, the probability of DB generation by direct sputtering is almost the same as that of insertion; however, in addition, the near-surface crystallinity is disrupted in most of the trajectories. The H@sub 2@ @super +@ ion bombardment under 20 eV, by contrast, can enhance the surface reactivity by creating defects only in the top surface layer without damaging the crstallinity of the underlying silicon.

9:40am **TF-WeM5 Low Temperature Growth of 2D Pb Islands on Si(111)7x7 Surfaces***, **C.S. Chang**,* Academia Sinica, Taiwan, ROC*; S.H. Chang,* National Tsing Hua University, Taiwan, ROC*; W.B. Su, C.M. Wei,* Academia Sinica, Taiwan, ROC*; L.J. Chen,* National Tsing Hua University, Taiwan, ROC*; TienT. Tsong,* Academia Sinica, Taiwan, ROC

Lead (Pb) is known to grow on Si(111) with the Stranski-Krastanov (SK) mode at room temperature. With the variable temperature scanning tunneling microscopy, we study the low temperature growth of Pb films on the Si(111)-7x7 surface from T ~40 K to 200 K. The islands are formed after the completion of the wetting layer and display peculiar properties that cannot be categorized into any of the conventional growth modes. Their tops are all very flat and even more surprisingly, they prefer to grow into some discrete thicknesses corresponding to 4, 7 and 9 atomic layers. Among them, that equivalent to seven atomic layers is especially dominant. While the stress in heteroepitaxy may be the only dominant factor for a thick film and hence causes the film to form into 3D islands, for a thin film some other effects may be in play to counterbalance the stress. One of such effects is the "quantum size confinement", which could reduce the system energy due to quantization of the confined electrons in the film. Preliminary ab initio calculations seem to support this theory.

10:00am **TF-WeM6 Modeling of Cluster Ion-Surface Interactions with Full Inclusion of Internal Degrees of Freedom***, **K.J. Boyd**,* University of New Orleans*; A. Lapicki, S.L. Anderson,* University of Utah

Molecular dynamics simulations with embedded atom or tight binding moment approximation potentials are used to investigate the interactions of small cluster ions (N<50) with metal surfaces. The simulations are performed at constant target temperature, with the cluster initially thermostatted independently. This allows the internal vibrational and rotational degrees of freedom of the cluster to be treated properly. At room temperature, the vibrational energy content of a 50 atom cluster may be several eV, which is comporable to the translational energy of the cluster. The rotational energy at room temperature is much lower, but the effect of cluster rotations is to change the momentum of cluster atoms such that they impinge at non-normal incidence on the target. This non-normal momentum component may alter the dynamics of cluster deposition by changing the fragmentation and penetration behavior.

10:20am **TF-WeM7 Extension Velocities for Level Set Based Surface Profile Evolution***, **D.F. Richards**, S. Sen, M.O. Bloomfield, T.S. Cale,* Rensselaer Polytechnic Institute

Level set based front-tracking methods represent an attractive alternative to more traditional node and segment based approaches to tracking interface motion. Level set methods avoid many topological difficulties which arise in node-moving schemes and are easily extended to three dimensions. However, level set methods also require knowledge of the speed function at every point in the solution domain. This is a somewhat troublesome requirement for profile evolution models since the interface speed may have no physical meaning at points that are not on the surface. The solution to this problem is to formulate extension velocities that in some way extrapolate speeds from the interface to other points in the solution domain. We compare several different methods for determining extension velocities and discuss the characteristics of node and segment approach that are helpful in calculating extension velocities.

10:40am **TF-WeM8 Models of Electrochemical Deposition of Copper Thin Films:The Effect of Leveling Agents***, S. Soukane, **T.S. Cale**,* Rensselaer Polytechnic Institute

As device sizes decrease, the ability of electroplating to create conformal films in deep features make it very attractive. Especially beneficial in interconnect applications is the "leveling" effect of certain organic additives. With the use of these leveling agents, electroplating offers the possibility of a superfilling effect, leading to void-free structures. This effect is often attributed to the inhibition of plating along feature sidewalls. Much feature-scale modeling work has been focused on reproducing the effect of the additive during deposition. The inhibition has been assumed to be due to operation at a mass transport-limited rate that allows the leveling agent to be completely depleted in the region near the surface. This may be a good assumption if the agent is highly reactive and used in quantities on the order of hundreds of ppm. Its inhibiting effect is usually correlated to the expression of the current density by a factor that is a function of the leveling agent flux to the surface. This approach limits the opportunities to look for explanations via chemical mechanisms. We show that the leveling effect can be explained via a more detailed chemical mechanism involving adsorbed species. We present a feature-scale model coupling the potential and concentration fields via the current density at the feature surface, together with a chemical mechanism involving surface species. In this chemical mechanism, copper ions go through two successive irreversible reactions. The first step is a charge transfer reaction, leading to an adsorbed copper species on the surface. The second is much faster, consisting of the adsorbate reduction and insertion into the film. It is assumed that the leveling agent is completely transformed on the surface to new species that play the important roles in the inhibition effect. These proposed surface species can undergo slow desorption reactions or can be incorporated in the solid at a rate much slower than copper insertion.

Vacuum Technology
Room 201 - Session VT-WeM
Sorption Processes and Leak Detection

Moderator: J.F. O'Hanlon, University of Arizona

8:20am **VT-WeM1 The United States Constitution and Vacuum Technology*, C.R. Tilford,*** Consultant, U.S. **INVITED**

The Charters of Freedom, the official copies of the United States Declaration of Independence, Constitution and Bill of Rights, were hermetically sealed in 1952 in glass and lead encasements filled with humidified helium. Deterioration of the inside glass surfaces has become evident in recent years, and is believed due to elevated water vapor concentrations, which can also be a direct threat to the parchment documents. The National Archives and Records Administration and the National Institute of Standards and Technology have undertaken to construct new encasements that will keep oxygen concentrations below 0.5% over 100 years, maintain a stable humidity level, and include mechanical and broadband optical access for gas sampling and spectroscopic monitoring. Prior to disassembly of the existing encasements, gas samples are extracted for humidity measurement and mass spectrometric analysis. This project presents several difficult vacuum technology challenges, including hard-sealing large glass windows to lightweight structures (for public viewing of the documents), helium leak testing the sealed encasements without evacuation, measuring humidity of small-volume gas samples, and extracting clean samples from the small-volume solder-sealed encasements. In all cases the solutions are constrainted by the absolute necessity to avoid perturbing the documents or over-stressing the lightweight encasements. To date, the gas sampling and reencasement process has been carried out for three pages of the Constitution. This talk will describe the vacuum techniques used and present the experiences and results to date.

9:00am **VT-WeM3 Measurements of Photon Stimulated Desorption from Thick and Thin Oxide of KEKB Collider Copper Beam Chambers and a Stainless Steel Beam Chamber@footnote 1@*, C.L. Foerster,*** *C. Lanni,* Brookhaven National Laboratory*; K. Kanazawa,* KEK, Japan

Photon Stimulated Desorption(PSD) from KEKB factory copper chambers was measured at the National Synchrotron Light Source(NSLS), located at the Brookhaven Laboratory. The KEKB is an asymmetrical collider recently constructed in Ibaraki, Japan. The collider utilizes two UHV ring chambers, one for a 3.5 GeV positron beam and the other for a 8 GeV electron beam, for B-meson studies. Two each, one meter long, 94mm inner diameter, chemically deoxidized copper beam chambers with conflat end flanges, were provided by KEKB to the NSLS, for measurment of PSD. PSD and specular reflection were measured on NSLS VUV ring beamline U9a. It has been reported that a high temperature air bake on large stainless steel vacuum systems reduces the need for a vacuum bake. To determine the effect of surface oxide, following the initial PSD measurment, the chambers were chemically cleaned and then oxidized in air for a week at 250 °C. PSD was remeasured after the air bake. A similar process and measurment was performed on a stainless steel beam chamber, with the exception of oxidation at 450°C. After the chambers were installed on beamline U9a, they were exposed to a minimum of 10@super23@ photons direct from the source having a critical energy of 595 eV, striking at an incident angle of 100 mrad. The major PSD yields for hydrogen, carbon nonoxide, carbon dioxide, methane, and water vapor are reported as a funtion of accumulated photon flux, incident surface oxide, and chamber preparation. The results are compared with other PSD measurments on NSLS beamlines and those of other laboratory publications for copper and stainless steel. @FootnoteText@ @footnote 1@Work performed under the auspices of the U.S. Department of Energy, under contract DE-AC02-98CH10886.

9:20am **VT-WeM4 Study the Exposure Dose-Dependent Photon Stimulated Desorption Phenomena*, G.Y. Hsiung,*** SRRC, Taiwan*; K.-Y. Young,* Institute of Nuclear Science, NTHU, Taiwan*; Y.J. Hsu,* SRRC, Taiwan*; J.-R. Chen,* SRRC and Institute of Nuclear Science, NTHU, Taiwan

The photon stimulated desorption (PSD) is studied by using the synchrotron radiation white light of critical energy at 2.14 keV from the 1.5 GeV Taiwan Light Source (TLS). The samples of various materials, e.g. aluminum alloys, OFHC, etc. are installed in a chamber at a beam line of SRRC for exposure measurement. The sample is water cooled during the exposure to the synchrotron light that the variation of temperature on the surface is < 0.2 degree C. A quadrupole mass spectrometer is used to measure the desorbed gas molecules by PSD in the exposure chamber. The result shows a decrease of the PSD-rate for each gas after a long time exposure of photon beam on the samples. The measured photoemission yield on the sample during exposure also decreases. The curves of pressure rise of each PSD-gas versus the time during the exposure show various kinds of trend with different time lag of the peak. The desorbed molecules including H2O, O2, CO, and CO2, have the time lag longer than those of H2 and hydrocarbon molecules. The longer beam dose exposed on the sample, the longer time lag of PSD peak trended. The phenomenon of exposure dose-dependent PSD relates to the surface condition of the exposed samples. A Secondary Ion Mass Spectroscopy (SIMS) system is built in the exposure chamber to assist the in-situ surface characterization. The correlation between the yield of both PSD and photoemission and the surface concentration during and after the exposure will be compared. The phenomenon of exposure dose-dependent PSD is described and compared.

9:40am **VT-WeM5 Study of Desorption of Carbonaceous Gas Molecules from Copper Surfaces under Electron Bombardment*, M. Nishiwaki,*** The Graduate University for Advanced Studies, Japan*; S. Kato,* KEK, Japan

Adoption of oxygen free copper has been recently begun to vacuum chambers of particle accelerators such as the KEKB accelerator that is a two ring electron-positron collider. Due to irradiation of the energetic particles and/or exposure to residual gas, however, the copper surface composition should be easily altered and consequently would give instable vacuum property because the passive surface cannot form on copper material which is different from other materials with passive surface such as stainless steel and aluminum. In this study, we aim to make clear about the mechanism about the adsorption and desorption on the copper surface using some isotope gas species. The copper surfaces to which some surface treatments were carried out were exposed to isotope gas species of @super 13@C with a known quantity in an ultra high vacuum. Afterwards, electron stimulated gas desorption (ESD) rates from these sample surfaces were measured using throughput method with a calibrated residual gas analyzer quantitatively. By using the isotope gas, desorbed gas under electron bombardment from the surface on which @super 13@C related gas molecules adsorb can be distinguished from desorbed @super 12@C related gas molecules which consist of diffused carbon atoms from the bulk since @super 13@C atoms do not exist in the bulk. Preliminary experimental results showed that enhancement of carbon diffusion to the surface under the electron bombardment occurred at a high sample temperature. This might suggest that the origin of carbon in the carbonaceous desorbed gas molecules such as CO and CH4 is not the top surface but the bulk possibly in a electron penetoration depth. Surface characterization of the copper materials will be also done using x-ray photoelectron spectroscopy in the adsorption and desorption processes of the isotope gas.

10:20am **VT-WeM7 Vacuum Characteristics of Sprayed Metal Films*, M. Minato,*** *H. Iwamoto,* Vacuum Metallurgical Co., Ltd., Japan

The need to reduce particles in semiconductor equipment or data storage equipment is increasing. In recent years, barrier and glue layers on shielding have been used to reduce particles generated in physical vapor deposition equipment. For this purpose, spray coatings are applied to shield components after contaminations are removed. Although the sprayed metal films are exposed to vacuum in a vacuum chamber, their vacuum characteristics have seldom been investigated. The conventional spray coatings are usually done under atmospheric conditions. In order to obtain a layer that has a better vacuum characteristic, spray coating in a chamber filled with an inert gas was developed. Outgassing characteristics of sprayed aluminum films and titanium films were investigated by using the conductance modulation method. Sprayed titanium film produced in an inert gas system showed a lower outgassing rate than that produced in an atmospheric condition.

10:40am **VT-WeM8 Edison's Vacuum Coating Patents***, R.K. Waits,* Consultant

Among the more than 1,000 patents bearing Edison's name are several for vacuum coating processes. In 1894 Edison was granted a patent on the "Art of Plating One Material on Another." The patent described coating by evaporation in a vacuum by direct resistance heating or arc heating, using a continuous current. Edison called the process "electro vacuous deposition." He prophetically wrote that "the uses of the invention are almost infinite". Edison also employed sputter deposition. In 1900, Edison applied for a patent on a "Process of Coating Phonograph Records." Issued in 1902, the patent describes using a "silent or brush electrical discharge" produced by an induction coil. Edison had found a way, perhaps accidentally, to use high-voltage alternating current to deposit a metal; the pressure was higher and deposition was by sputtering rather than evaporation. The National Phonograph Company, one of Edison's many enterprises, used the sputtering process to deposit a thin layer of gold on wax phonograph cylinder masters that could then be electroplated to form molds to mass-produce celluloid duplicates. The resulting cylinders were touted as "Gold Moulded." The method was used for 20 years, from 1901 to 1921. It enabled the reproduction of cylinder grooves less than 0.001-inch deep at a density of 200 grooves per inch. From 1913 to 1921, 10-inch-diameter Edison Diamond Disc phonograph records were made using the same method. Sputtering was abandoned as it could not be scaled up to produce the 12-inch discs that were introduced in 1927.

Biomaterial Interfaces
Room Exhibit Hall C & D - Session BI-WeP
Poster Session

BI-WeP1 Hydroxy-containing Amino Acid Derivatives Adsorbed on Gold*, J. Svensson,* ***A. Borgh****, K. Uvdal, B. Liedberg, P. Konradsson,* Linköping University, Sweden

More than 10% of the proteins in the body are involved in phosphorylations. As a phosphate group is attached to serine, threonine or tyrosine, the protein changes its conformation. This change in conformation is often ascribed to neutralization of charges, i.e. by electrostatic interactions. The attachment also effects the surrounding water structure and this change in water structure could be the reason to conformational changes. We describe here the preparation of a series of model surfaces, based on self-assembly on gold, in order to study the surrounding water structure. Surface characterization is performed using infrared reflection-absorption spectroscopy (IRAS), ellipsometry, contact angle goniometry and X-ray photoelectron spectroscopy. The molecules are found to form highly ordered monolayers and the thicknesses of the monolayers are in good agreement with expected values from space filling models. Water structure studies are performed using IRAS and temperature programmed desorption.

BI-WeP2 Template Stripped Gold Surfaces for Advanced Biological Applications*,* ***M. Hasselblatt****, F. Zaugg, P. Wagner,* Zyomyx, Inc.

Template Stripped Gold (TSG) surfaces have been used extensively as a source for ultra-flat substrates. Thin Gold films evaporated on a freshly cleaved mica surface at elevated temperatures are glued onto a substrate to allow the removal of the mica. The gold films accessible this way exhibit sub-nanometer roughness over areas larger than micrometers. Here, we review methods for preparing these surfaces. Also, we present a novel bonding technique, in which Indium solder is used. Such sandwiches resist all common organic solvents and aqueous buffers typically used for biologically relevant experiments.

BI-WeP3 Macroporous TiO@sub 2@ Films Prepared on Ti Surfaces with Predefined, Micron-Sized Pores*,* ***F.A. Akin****, L. Hanley,* University of Illinois at Chicago

Surface morphology is critical to the biocompatibility of hard tissue implants, such as those used for dental and orthopedic applications. Porous bioceramics are commonly used for some applications due to their ability to encourage bone ingrowth, but they lack the physical strength required for load bearing applications. A new method is described for preparing thick, macroporous TiO@sub 2@ films on Ti surfaces with pre-defined, micron-sized pores. Scanning electron microscopy shows that these pores 1) are controlled to a narrow size range by the synthetic process, 2) can be prepared from 0.5 to ~100 µm diameter, and 3) are interconnected within the film. The films are ~0.1 mm thick and strongly adherent to the Ti surface. X-ray photoelectron spectra indicate that these films can be prepared as elementally pure TiO@sub 2@. X-ray diffraction indicates that the films are monophasic as either anatase or rutile TiO@sub 2@. Scanning electron microscopy following immersion in Ringer's solution for several days shows that the films are not expected to undergo resorption following implantation. The effect of pore size is examined for fibroblast proliferation and spreading in vitro. These macroporous TiO@sub 2@ films should allow applications that combine the favorable mechanical properties of Ti metal implants with the tissue engineering enhancements possible with porous bioceramics.

BI-WeP4 Photovoltaic Characteristics of bR/p-Silicon Heterostructures using Surface Photovoltage Spectroscopy*, L.S. Li, T. Xu, J. Jin, Y.J. Zhang,* Jilin University, P.R. China*;* ***T.J. Li,*** Jilin University, P.R. China, P.R.China*; B.S. Zou, J.P. Wang,* Georgia Institute of Technology

In bR-based photoelectric devices, the highly efficient electric response can be obtained only when the bR molecules have a nonrandom orientation. LB technique enables molecular-order organization that can be used to incorporate bR into devices. As a prototype molecular electronic device, it will be more significant to deposit oriented bR films on a silicon substrate. In this paper, orientated bR films were deposited on the hydrophilic and hydrophobic silicon substrates using the LB technique. The cytoplasmic (CP) or extracelluar (CE) surface of bR face the silicon directly, giving oriented patterns of Si/CP-EC and Si/EC-CP, respectively. The photovoltaic features and interfacial charge separation of p-Si/bR/ITO heterostructure are studies by surface photovoltage spectroscopy (SPS). The different photovoltage response values obtained are due to the nonrandom orientation of bR in the LB films on the hydrophilic versus hydrophobic silicon substrates. The photovoltage response value versus external potential of the p-Si/CP-EC/ITO heterostructure shows an obviously rectifying behavior. Compared with the p-Si/ITO heterostructure, the response value of SPS increases more rapidly in the case of the positive external potential.

BI-WeP5 Patterning Hybrid Surfaces of Proteins and Supported Lipid Bilayers*,* ***L.A. Kung****, L.C. Kam, J.S. Hovis, S.G. Boxer,* Stanford University

Two methods for patterning surfaces with supported lipid bilayers and immobilized protein are described. First, proteins are used to fabricate corrals for supported lipid bilayers. Poly(dimethylsiloxane) (PDMS) stamps are used to deposit arbitrarily-shaped patterns of thin layers of immobilized protein onto glass surfaces. This is followed by formation of supported lipid bilayers via vesicle fusion into the regions that are not coated with proteins. Second, supported bilayer membranes are blotted to remove patterned regions of the membrane,@footnote 1@ and the blotted regions are filled in (or caulked) with protein from solution. In both cases, the lipid bilayer regions exhibit lateral fluidity, but each region is confined or corralled by the protein. These two methods can be combined and used iteratively to create arrays with increasing lateral complexity in both the fixed protein and mobile supported membrane regions for biophysical studies or cell-based assays. @FootnoteText@ @footnote 1@ Hovis, J. S.; Boxer, S. G. Langmuir 2000, 16, 894-897.

BI-WeP6 Individually Addressable Solid Supported Membranes Formed by Micromolding in Capillaries*,* ***S. Kuenneke****, A. Janshoff, H. Fuchs,* WWU Muenster, Germany

The formation of spatially individually addressable, patterned biomaterial on surfaces is of paramount interest for the development of biosensors, combinatorial libraries, and high-throughput systems for pharma screening. Particularly, the combination of high resolution scanning devices with lithographically structured biomolecules is advantageous if the amount of biomaterial is limited or if the number of surface reactions is vast. The most versatile matrix for embedding and immobilizing natural and artificial receptor molecules such as functionalized lipids or proteins are solid supported membranes. Here we present a new type of microstructured membrane compartments, which are individually addressable by the operator on a common substrate on a nanometer to micrometer scale. The membrane segments are designed to be accessible to all available microscopic techniques and surface analysis tools. We developed a general procedure to generate patterned lipid bilayers by using a three dimensional network of capillaries as provided by microfluidic networks. The fluidic network (elastomer stamp) was formed from polydimethylsiloxane (PDMS) using an appropriate master displaying the inverted desired structure, which can be conveniently obtained by optical lithography of silicon wafers. Lipid bilayers were deposited by fusing unilamellar vesicles on the hydrophilic glass substrate. Visualization of the liposome flow in the capillaries and the formed planar bilayers was performed using a confocal laser scanning microscope. The planar bilayers were subsequently imaged by means of scanning force microscopy revealing a typical height of 4-6 nm.

BI-WeP7 Vesicle -> Supported Bilayer Transformation Kinetics; Influence of Support Material, Vesicle Size and Temperature*,* ***E. Reimhult****, F. Höök, B. Kasemo,* Chalmers University of Technology, Sweden

Supported phospholipid bilayers (SPB) on a solid surface are biologically functional components of high current interest, e.g., for biosensors, tissue engineering, and basic science (Sackman, Science 271:43 (1996); Stelzle et al., J. Phys. Chem. 97:2974 (1993)). We have recently reported the kinetics of SPB formation from sonicated, unilamellar vesicles (SUV) of average size 25 nm, on a SiO@sub 2@ support, using the quartz crystal microbalance - dissipation (QCM-D) technique (Keller and Kasemo, Biophysical Journal 75:1397 (1998); Keller et al., Phys. Rev. Lett. 84:5443 (2000)). Several interesting questions arose from the latter results; how does the vesicle -> bilayer transformation kinetics depend on the vesicle size, on temperature, and on the support. In the present study we are addressing these questions, whose answers are important for future sensor, biomaterial and micro-patterning applications. Already obtained results reveal a (vesicle) size-dependent kinetics, where also the end result (the final bilayer) may have different properties for different sizes of extruded unilamellar vesicles (EUV). The dependence on temperature is currently studied and will be reported. An exploratory study shows a strong temperature dependence for the vesicle -> bilayer transition. Different surfaces also cause different kinetics. So far, SiO@sub 2@ surfaces have been the dominating support used to promote complete bilayer formation. Vesicle adsorption, but no bilayer formation, is observed for oxidized Ti and Au surfaces , while partial bilayer formation may occur on Pt. The above results constitute a platform from which more complex functional supported bio-membranes can be constructed (Höök et al, to be published).

BI-WeP8 Use of Bacterial Adhesion Related and Collagen Related Peptides to Bind and Orient Fibronectin on Surfaces*, **U. Klueh,** D.L. Kreutzer, J.D. Bryers,* University of Connecticut, Schools of Medicine and Dentistry

Although small molecular weight proteins and peptides have been bound and oriented on surfaces, little is known about orienting large molecular weight proteins, (e.g. FN) on surfaces. Recently two classes of peptides have been shown to bind to FN in vitro, i.e. Collagen Related Peptides (CRP) and Bacterial Adhesion Related Peptides (BARP). We hypothesized that if these peptides could be used to not only bind, but also orient FN on surfaces. We further hypothesized that antibodies to specific regions of the FN molecule can be used to demonstrate the orientation of the peptide bound FN. CRP and BARP peptides were synthesized commercially and immobilized on polystyrene surfaces. FN was nonspecifically bound to polystyrene by physisorbtion. FN binding to the immobilized peptides was quantitated using monomeric/functional @super125@I-FN and polyclonal antibodies to FN. Orientation of the bound FN was demonstrated using antibodies specific to the amino (anti-N) and carboxyl (anti-C) termini of FN. Polystyrene immobilized CRP and BARP bound 125 ng/cm@super2@ and 94 ng/cm@super2@ of FN. Little FN bound to control (non-peptide containing) surfaces 5 ng/cm@super2@. FN bound to CRP and BAR peptide bound anti-FN and anti-C antibodies but did not bind significant levels of anti-N antibodies, compared to randomly bound FN (i.e. physisorbed FN). Additionally, we demonstrated that although CRP did inhibit FN binding to immobilized collagen, BRAP did not. Finally we demonstrated that the uses of monomeric/functional FN was critical in establishing FN monolayers on CRP or BARP coated surfaces. Our results not only demonstrate the ability of CRP and BAR peptide to specifically bind and orient fibronectin in monolayers, but also underscore the usefulness of specific polyclonal and monoclonal antibodies to characterize the binding and orientation of FN on these surfaces.

BI-WeP9 Conformational Changes of the Extracellular-matrix Protein Fibronectin Induced by Force Spectroscopy*, **Y. Oberdoerfer,** H. Fuchs, A. Janshoff,* WWU Muenster, Germany

Since its invention, force spectroscopy by SFM became a powerful instrument to study the structure, mechanism and behaviour of polymers. Especially for biopolymers it is important to be able to perform these studies in a native environment, an advantage which is provided by SFM. In this work we studied conformational changes of the extracellular-matrix protein fibronectin and provide direct proof for the presence of the protein on the cantilever verifying whether it was pulled on the polymer or not. Fibronectin is a modular protein consisting of three different FN-domains: FN I, FN II and FN III. These three domains differ in the number of their appearance in one single fibronectin polymer and also in the number of amino-acids. Extending fibronectin during a force-measurement results in unfolding events of single domains can be distinguish in a force-curve due to the elongation of the polymer itself and also the absolute number of unfolded domains. In this way it is possible to determine whether a FN I-, FN II- or FN III-domain was unfolded. Another topic that should be presented is the possibility to make an elemental mapping of a cantilever surface by means of SIMS and SNMS to determine if the investigated polymer was attached to the probe. With this kind of measurement one can verify if unfolding events occurring in a force-curve arise from the substance itself or any kind of contamination.

BI-WeP10 Observation of Bone Fracture Healing Processes by Atomic Force Microscopy*, **V. Baranauskas,** I.G. Freitas, Z. Jingguo, M.A. Cruz-Hofling,* Universidade Estadual de Campinas, Brazil

Atomic Force Microscopy (AFM) was used to study the healing process of bone surgical fracture in rats. We used young male adult rats (Wistar), with corporal masses between 250 and 300 grams. Each fracture was provoked by drilling a 2 mm diameter hole in one cortical tibia surface. The healing course was monitored at 8, 15 and 22 days after the fracturing. AFM images, at different magnifications, allowed to the identification of the time dependence of the osteoblastic activity, measured by the increase in the primary bone trabeculae surface and the increase in the synthesis and organization of collagen fibers of the bone matrix. Characterization of the natural recovery of the damaged bone tissue by AFM is potentially of great importance because it allows the comparison of natural recovery and the recovery induced by medicines or other cures.@footnote 1@ @FootnoteText@@footnote 1@ I. G. F. Freitas, V. Baranauskas, M. A. Cruz-Höfling, Laser effects on osteogenesis, Applied Surface Science 154-155 (2000) 548-554.

BI-WeP11 Dielectric Characterisation of Aminal Bone*, **S. Mohiuddin,*** King Saud University, Saudi Arabia

The investigation deals with the electrical properties of bovine bones. Dielectric constant, dielectric loss, conductivity and resistivity are determined in bovine tissues are lossy dielectric. They are partly polarisable and partly conductive. The influence of calcium phosphate on the electrical behavior of bone is also studied. Data of electrical parameters of bovine scapula, rib and femur bones reveal the considerable variation in different bones samples and also in different specimens of the same bone, obtained from various parts of the bone. This may be attributed to the inhomogeneous deposition of calcium phosphate and water content of the bones. The sharp fractional changes in dielectric constant and resistivity with the water content of bone specimens suggests that the electrical parameters are very sensitive to free water present in bones in contrast to ultrasonic and mechanical properties. Influence of water on electrical behavior is specific to bone because of the fact that mineral content of the bone is found to be in different proportions which also effects the electrical make up of the bone. The three parameters namely water content, mineral content (calcium phosphate) and orientation of the collagen fibers with respect to the applied electric field, play an important role in influencing the electrical parameters conductivity of the bone tissue, when measured at the bulk, level.

BI-WeP12 TOF-SIMS Characterization of Nucleic Acid Biosensors*, **H.F. Arlinghaus,** M. Ostrop, O. Friedrichs, U. Gunst,* Physikalisches Institut der Universität Münster, Germany

In recent years, biosensors consisting of immobilized oligodeoxynucleotides (ODN) have been a subject of growing interest for DNA sequencing and clinical diagnostics. We have used static TOF-SIMS and temperature-programmed SIMS (TP-SIMS) to examine in detail the immobilization process of ODNs, which were directly bound to Au- and Ag-surfaces by thyol-linkers. Protonated (M+H)@super +@ and deprotonated (M-H)@super -@ signals of the different ODNs and bases as well as phosphate ions were used to monitor the ODN concentration. The influence of ODN concentration and immobilization time on the immobilization process was investigated. It was found that the maximum intensity for characteristic ODN peaks was obtained using a 1 µM solution and an immobilization time of 24 h. According to our estimate, the surface coverage under these conditions should be close to a monolayer. Measurements of how surface structure affects the process of immobilization showed a higher intensity of the characteristic ODN signals and a less homogeneous oligonucleotide layer with increasing surface roughness. TP-SIMS was used to measure the thermal stability of the immobilized layers. The data show that the characteristic ODN fragment ions start to decrease at a temperature of about 150° C, with differences in the point of onset for the different bases. It can be concluded that the combination of TOF-SIMS and TP-SIMS is a powerful technique to examine the complexity of the immobilization and hybridization processes of nucleic acid.

BI-WeP13 Characterization of Multi-Component Adsorbed Protein Films by ToF-SIMS*, **M.S. Wagner,** D.G. Castner,* University of Washington

Characterization of the adsorbed protein films on biomaterial surfaces is needed for the rational design of biomaterial surfaces. Many surface analysis techniques, however, do not provide efficient means for analysis of these surfaces. Time of Flight Secondary Ion Mass Spectrometry (ToF-SIMS) is an excellent technique for the analysis of complex protein films due to its chemical specificity and surface sensitivity. The ToF-SIMS fragmentation pattern is highly complex due to the heterogeneity of the protein composition and the absence of unique, identifying peaks from protein to protein. Analysis of such complex spectra requires the use of multivariate analysis methods to effectively use the ToF-SIMS data. Therefore, we have utilized ToF-SIMS in conjunction with Partial Least Squares (PLS) regression to estimate the surface compositions of binary and ternary adsorbed protein films. Using only the pure component ToF-SIMS spectra, PLS was able to estimate the relative concentrations of the proteins on the surface. Furthermore, using a set of standard protein spectra, Principal Components Analysis (PCA) was able to provide insight into how the composition of a protein film adsorbed from 1% bovine plasma varied with adsorption time. PCA of the ToF-SIMS spectra revealed a shift from mostly fibrinogen to mostly immunoglobulins over the course of two hours. ToF-SIMS/PCA has the tremendous advantage that several proteins can be analyzed in a single experiment, given the appropriate standard spectra. The combination of multivariate analysis methods and ToF-SIMS greatly simplifies the analysis of adsorbed protein films.

BI-WeP14 Correlation of Cell Health with Protein Layer Thickness on Modified Surfaces Characterized by XPS, XAS, and Morphological Analysis*, **H.E. Canavan**,* The George Washington University*; W.E. O'Grady,* Naval Research Laboratory*; J.J. Hickman, D.E. Ramaker,* The George Washington University

The interactions of biomolecules with surfaces are of significant interest in the areas of biocorrosion, bio-implant rejection, and biological fluid interactions with MEMS devices. This interaction may dictate the health of nearby cells by either a) continuing cell function as normal, b) continuing cell function in an abnormal manner, or c) cell death. In the work presented here, the biomolecular interaction is altered via prior surface modification with Self-Assembled Monolayers (SAMs) of amines or fluorinated compounds. The surfaces are then introduced into cell culture using cardiac and other cells. The interaction of the derivatized surfaces with proteins and cells are investigated to see a differential response to the modifications. X-ray Photoelectron Spectroscopy (XPS) is used as an analytical technique to characterize the modified surfaces of the silanes prior to cell culture. XPS is also used characterize the protein deposition layer thickness which serves as an indication of cell function and health. Optical microscope images of cells grown on different substrates are compared to time-dependent XPS results to correlate cell morphology with protein layer thickness. Sulfur K-Edge X-Ray Absorption Spectroscopy (XAS) data are used to monitor the extent of S-C, S-O, and S-H bonds, which affect the character of the extruded proteins.

BI-WeP15 Soft X-ray Spectromicroscopy of Protein Adsorption on Polyurethanes*, **C. Morin**, A.P. Hitchcock, I.N. Koprinarov, R. Cornelius, J.L. Brash,* McMaster University, Canada

New quantitative techniques for chemical microanalysis which allow detailed study of protein polymer interactions are required for biomaterial interface optimization. We are particularly interested in identification of possible preferences of first sites of protein attachment to polyurethane polymers used in blood contact medical applications. We are exploring Scanning Transmission X-Ray Microscopy (STXM) and Photoemission Electron Microscopy (PEEM) in this context. These techniques use near edge X-ray absorption spectroscopy (NEXAFS) for chemical identification. Both techniques have been used to map albumin and fibrinogen adsorbed on various polymer surfaces. As an example, STXM was used to study protein adsorption from a 0.1 mg/ml albumin solution onto a TDI-based, high-ether polyurethane film (~100 nm thick) which had submicron phase segregated regions of a highly aromatic polyisocyanate polyaddition product (PIPA) reinforcement material. Image sequences recorded throughout the C 1s and N 1s regions were used to generate composition maps by fitting the spectrum at each pixel to spectra of pure reference materials. The strong amide carbonyl resonance at 288.2 eV provides a sufficiently strong signature of protein to allow mapping down to monolayer levels even though the STXM results average over the full thickness of the polymer and protein sample. PEEM studies on similar materials provide greater surface sensitivity but are complicated by high sensitivity to topography as well as charging artefacts. Results from the two techniques will be compared to illustrate the strengths and weakness of these soft X-ray spectromicroscopy techniques when applied to biomaterials problems. X-ray microscopy is carried out at the Advanced Light Source (supported by DoE under contract DE-AC03-76SF00098), supported financially by NSERC (Canada).

BI-WeP16 A Novel Approach to Studying Structures and Orientation at the Protein-Self Assembled Monolayer Interface*, **L.F. Pardo**, T. Boland,* Clemson University

Self-assembled monolayers (SAMs) have become an important tool in protein adsorption studies, partly because they represent chemically, well-defined model systems. However, specifics on how the structure and orientation of both the SAM and protein change during adsorption in situ remain unknown. The purpose of this study is to quantify these changes via analysis of protein adsorption onto SAMs by a novel technique using Evanescence Reflection Spectroscopy (ERS). This technique allows in situ characterization of the surface chemistry, providing quantitative information on structure and orientation at the interface only. In this study, model proteins, (polyserine and fibrinogen) were adsorbed onto, -OH, -COOH, and CH3 terminated SAMs of hexadecanethiols on gold. The surfaces were then characterized by FTIR and ellipsometry. The IR measurements reveal significant differences were between protein structures in dry and wet states. The spectra of polyserine in the dry state show only amide II stretch (1507 cm-1) while the amide I stretch is absent implying that the polyserine lies flat on the SAM surface. Analysis of the IR spectra measured in PBS solution depicting peaks in the Amide I and II regions showed that polyserine extends away from the surface under aqueous conditions. Furthermore, information on the secondary structure of the solvated proteins adsorbed to the various SAMs was attained. The resulting of protein-SAM interfaces are dynamic and will undergo structural changes, desorption or surface reactions. The structural characterization of protein SAM interactions will be helpful when designing templates for tissue engineering applications.

BI-WeP17 Microbial Adhesion on Polymer: Role of Morphological and Chemical Properties in the Micro-organism Behaviour*, **M. Anderle**, R. Canteri, E. Carli, S. Janikowska, A. Lui, C. Pederzolli, G. Speranza,* ITC-irst, Italy*; D. Maniglio, C. Della Volpe,* Università di Trento, Italy

Infections caused by implanted polymeric devices (especially catheters) have an increasing importance in the medical routine (up to 40% of nosocomial infections). The critical event in the pathogenesis of foreign body infection is the adhesion of the micro-organisms to the biomaterial surfaces followed to the colonisation. In order to achieve a deeper understanding of the molecular-level interactions between catheters and biological system, the aim of this work is to study the physicochemical properties of the polymeric surface and their influence on the microbial adhesion and colonisation. Some common polymers produced by standard processing methods have been analysed by dynamic contact angle (DCA), X-ray Photoelectron Spectroscopy (XPS), Time of Flight Sims (TOF Sims) and Scanning electron microscope (SEM). Moreover biological tests were performed to determine the degree of gram+ and gram- bacterial adhesion on these surfaces. The results show relevant deviation of the contact angles from the expected values. These results are only partially explained by the XPS and the TOF Sims analysis. XPS and TOF Sims spectra revealed normally contaminated polymer surfaces and deviations from the nominal composition also after accurate cleaning, performed using different methods. In particular oxidation of the polymer surface occurring probably during the moulding process and other factors are able to introduce chemical functions which lead to a surface chemistry significantly different from the expected one. High value of contact angle and unexpected values of bacteria adhesion can be explained taking into account the presence of basic functions and the roughness of the surface. These elements decrease the differences expected on the basis of the acid, basic or dispersive characters of the examined polymers.

BI-WeP18 Functionalised Plasma Polymers for Control of Cell Attachment*, **J.M. Kelly**, R. Daw, R.D. Short,* University of Sheffield, UK

Surface chemistry is known to be an important factor in mediating cell attachment and subsequent activity on materials whether in the context of an in vitro culture system, implanted biomaterial or tissue engineered construct. In our studies on alcohol and carbonyl containing surfaces, cell attachment increased almost linearly with functional group concentration (up to 20-30%) whilst on carboxyl containing surfaces a low threshold concentration (approximately 5%) promoted excellent levels of cell attachment above which further increase of carboxyl concentration does not appear to promote greater cell attachment. Using a binary mixture of functional monomer (acrylic acid, methyl vinyl ketone or allyl alcohol) with a diluent hydrocarbon monomer (octa-1,7-diene), thin layers of polymer have been produced by radio frequency (RF) plasma deposition. Polymerisation took place at a pressure of 4x10@super -2@ mbar with the plasma supported by a 13.56 MHz, 2 W continuous wave power supply. X-Ray Photoelectron spectroscopy has shown the surfaces to contain hydrocarbon as well as hydroxyl, carbonyl and carboxyl functionality and that increasing the amount of functional monomer used in the plasma led to an increase of the corresponding functionality in the deposit. A rat osteosarcoma cell line (ROS 17/2.8) and human bone marrow cells were used for cell attachment studies. Cells were seeded at 3x10@super 4@ cells/cm@super 2@ and incubated for 3 h and 24 h in serum containing media. Cell attachment was quantified by direct counting after staining with methylene blue. Cell attachment studies are being carried out in parallel on self assembled monolayers containing similar ranges of functionality to allow comparison of plasma polymerised deposits with model surfaces.

BI-WeP19 Study of Protein Adsorption on Hydrophilic and Hydrophobic Polysiloxane Surfaces Modified by O@sub 2@ Plasma Technique*, **C. Satriano,*** University of Catania, Italy, Sweden*; F. Höök,* Chalmers University of Technology and Göteborg University, Sweden*; G. Marletta,* University of Catania, Italy*; B. Kasemo,* Chalmers University of Technology, Sweden

Thin films of a poly(hydroxymethyl)siloxane have been chemically modified by using the O@sub 2@ plasma technique at increasing treatment times ranging from 15 seconds to 10 minutes, with the applied power of 100 Watts and a residual gas pressure of 0.25 torr. The plasma-induced surface chemical modifications were investigated in situ by means of X-Ray Photoelectron Spectroscopy (XPS) for both the in situ samples and the samples aged in air and/or in water. By means of Static Contact Angle measurements the wettability properties of the unmodified and the O@sub 2@ plasma-exposed surfaces were investigated. The XPS results show that the compositional modification involves a dramatic decrease in the carbon content and the formation of [SiO@sub 4@] clusters, indicating a successive transition with treatment time from the original [SiO@sub 3@C] structure to [SiO@sub x@C@sub y@] phases. The contact angle measurements indicate that the plasma treatment changes the initial hydrophobic surface (@theta@ ~ 90°) of the polymer into a completely wettable surface, with @theta@ = 0-10° contact angle. After aging in water the surface is still completely wettable, while aging in ambient atmosphere produces a mild recovery in the contact angle values. These surfaces are currently subject to measurements of protein adsorption and of vesicle to supported membrane transformations, using QCM-D and other techniques. The results of these measurements and how they correlate with the XPS and wetting angle measurements will be presented.

BI-WeP20 Colloidal Lithographic Methods for Cell Culture Experiments*, **A.S. Andersson**, D.S. Sutherland, P. Hanarp, B. Kasemo,* Chalmers University of Technology, Sweden

The interaction of cells with surfaces can be modulated by the surface topography and chemistry on the micrometer and submicron length scale. Relatively recent evidence has shown that topography and chemistry on the nanometre scale can influence the functional behaviour of both protein molecules and selected cells. It is likely that the structural properties of a surface from the micron down to the nanometre and molecular scale are able to influence cellular behaviour, either directly or via an adsorbed hydrated protein layer. In order to systematically study the influence of surface properties on cellular behaviour methods to fabricate surfaces with defined and varied chemical and topographic architectures on a range of different length scales are required. A prime requirement of fabrication for cell culture experiments is that (by the standards of nanofabrication) extremely large areas of surface can be quickly fabricated. Colloidal lithographic methods have been developed to systematically fabricate nanometer features with defined size, shape and distribution over large areas in a single fabrication process. These methods utilise individual colloidal particles as a mask material for lithographic processing and have been used to create surfaces with a single type of topographic or chemical feature of defined size (available size in the range 10-200nm in all spatial dimensions). In combination with traditional photolithographic methods micrometer sized strips have been patterned with the nanometre-sized features to create surfaces with hierarchical chemical and topographic structures. These surfaces have been used in range of exploratory cell culture experiments.

BI-WeP21 Endothelial Cell Organization on Micropatterned Protein Surfaces*, **R. Daw**, T.N. Wight,* University of Washington*; R.B. Vernon,* Hope Heart Institute*; P.S. Stayton,* University of Washington

We have employed microcontact printing to investigate how spatial control of adhesive domains can direct the development of endothelial cell tubes for applications in tissue engineering and array-based sensors. Previous studies by Dike and co-workers showed that controlling adhesive geometries can dramatically affect endothelial cell fate and tube formation.@footnote 1@ Initial studies were directed toward comparing bovine aortic endothelial cell adhesion and activation on 5, 15 and 30 µm lanes of fibronectin (FN) versus laminin (LM) in the presence of 1 ng/ml of VEGF. Cells on LM tracks were able to migrate into intervening spaces of 20 µmm after 24 h. When the spaces between the lanes were increased from 20 to 80 µm cells remained adherent to the LM tracks except for those on the 5 µm tracks. Here, cells could spread between adjacent lanes. Endothelial cells were adherent to FN lanes throughout the range of pattern dimensions. A higher concentration of VEGF (10 ng/ml) stimulated migration off the patterned FN lines. FN lanes of 5, 15 or 30 µm were selected for subsequent studies directed toward defining the dimensionality of endothelial cell organisation into tubes. TEM showed that cells on tracks of 5 µm exhibited a significant arc of curvature and single endothelial cells encircled an organised fibrillar material to form tubes. Single tubes were also observed on 15 µm tracks but at this lane width, 2-3 cells organised together and circled a larger central fibrillar tube. These studies suggest that the composition of matrix proteins may play an important role in controlling endothelial cell development in confined geometries and that the organisation of endothelial cells into tube structures can be readily manipulated by controlling adhesive pattern dimensions. @FootnoteText@ @footnote 1@ Dike, L.E., Chen, C.S., Mrkisch, J.T., Whitesides, G.M., Ingber, D.E.; In Vitro Cell Devel. Biol. - Anim.; 35: 441-448; September 1999.

Incorporating Principles of Industrial Ecology

Room Exhibit Hall C & D - Session IE-WeP

Poster Session

IE-WeP1 Accurate Measurement for PFC by Mass Spectrometry using New Ionization*, M. Nakamura, K. Hino, T. Sasaki, **Y. Shiokawa,*** Anelva Corporation, Japan

To establish a method of accurate measurement for PFC is urgent global task. But, present methods by FT-IR and conventional mass spectrometry using electron impact ionization (EIMS) have serious problems: all kinds of by-products must be assumed before measurement and the quantitative results by the methods do not agree with each other. In order to overcome the problems, we have developed Ion Attachment Mass Spectrometry (IAMS) using new ionization@footnote 1@ and applied it to measurement of PFC. In IA MS, a Li@super +@ from heated Li-oxide emitter attaches moderately to a gas molecule. The excess energy caused by attachment is very small and is removed immediately owing to many collisions with other gases at 100Pa. Therefore, the gas with Li@super +@ a re not dissociated and becomes stable an ion as a whole. First, raw C @sub 4@F@sub 8@ without generating plasma was measured by IAMS. Quasi-molecule peak of C @sub 4@F@sub 8@Li appeared on the mass spectrum and any fragment peaks could not be found, whil e only fragment peaks appear by EIMS. Detectable limit of C @sub 4@F@sub 8@ was less than 1ppm. Other PFC gases such as C@sub 2@F@sub 6@, CHF@sub 3@ and SF@sub 6@ showed same results. Next, exhaust gases from dry etching system with generating plasma of A r, C @sub 4@F@sub 8@ and O@sub 2@ were directly introduced into IAMS and measured. Unreacted C @sub 4@F@sub 8@ and some expected by-products such as C@sub 2@F@sub 4@, CHF@sub 3@ were clearly confirmed from their quasi-molecule peaks. But, more than 10 kinds of unexpected by-products such as C@sub 2@H@sub 3@F@sub 3@, C@sub 3@H@sub 3@F@sub 5@, C@sub 4@OF@sub 8@ were detected, too. It seems likely that the existence of these unexpected by-products cause the disagreement between results by FT-IR and EIMS. @FootnoteText@ @footnote 1@ T.Fujii, Chemical Physics Letters 191 162 (1992).

MEMS

Room Exhibit Hall C & D - Session MM-WeP

Poster Session

MM-WeP1 Characterizing the Thermal Behavior of Thin Films Using Micromachined Cantilevers*, **H.-C. Tsai**, W. Fang,* National Tsing Hua University, Taiwan

The thermal stress is a very important factor of fracture for microstructure. In this paper, we exploit the micromachined cantilever to investigate the thermal behavior of the thin films. The thermal behaviors of thin films were characterized under two thermal loads including the thermal cycle load and the isothermal load. Thus, the variation of the thermal stress of thin film with the thermal loading time is studied. Moreover, the variation of the thermal strain rate of thin film with the film thickness is also discussed. In summary, the strain rate of thin film is proportion to the film thickness after the isothermal load test. On the contrary, the strain rate of thin film is in inverse proportion to the film thickness after the thermal cycle load test. In this study, the silicon dioxide cantilevers were fabricated through the bulk micromachining. The film to be characterized was then deposited on top of the cantilever to form a bi-layer beam. Since the thermal expansion coefficient (CTE) of the film and that of the silicon dioxide are different, the film will subject to stress during the thermal load test. The strain of the deposited film is determined by the deflection of the bi-layer beam. For the isothermal load test, the bilayer beam was heated by a heating stage. As to the thermal cycling load test, the sample was placed into a chamber that can set the variation of the temperature with time. In application, the thermal behavior of the sputtered Al film is studied. The Al film is under compression during heating since its CTE is larger than that of the silicon dioxide. As a result of isothermal load, the total compressive strain of the Al film was increased drastically in the beginning. However, the compressive strain of the Al film was gradually decreased after a certain heating time. It was obtained that the decreasing rate of the strain was proportional to the film thickness. For the thermal cycle load test, the variation of the strain of Al film with the number of thermal cycle was measured. We obtained that the compressive strain of Al film was drastically increased for the first 200 cycles, and then gradually decreased. According to this study, the thermal behaviors of thin films under the static and the dynamic loads are discussed. In addition, the film thickness will be an important factor for the thermal behaviors of thin film.

MM-WeP2 Electrical and Spectroscopic Characterization of Palladium Implanted Elevated Temperature Silicon Carbide Chemical Sensors*, **C.I. Muntele**,* Alabama A&M University*; P. McCarty,* University of Alabama, Huntsville*; I. Muntele, D. Ila,* Alabama A&M University*; J.J. Weimer, M.A. George,* University of Alabama, Huntsville*; D.J. Larkin,* NASA Glenn Research Center*; D.B. Poker, D.K. Hensley,* Oak Ridge National Laboratory

Silicon carbide is a promising material for creating microelectromechanical devices and integrated chemical sensors capable of working at room temperature as well as at high temperatures, and in harsh environments. This team has developed a unique miniaturized SiC chemical sensor that operates from room temperature to above the temperatures (300-500oC) of previously reported semiconductor based chemical sensors. To produce these sensors, we have implanted Pd ions at energies between 100 keV to a few MeV into the Si face of 6H-SiC at both room temperature and at 5000C. The peak concentration of implanted Pd was kept between .01% to 10% of the host. The electrical properties of fabricated sensors were measured at room temperature up to 500oC. We will discuss both the preparation and characterization of these sensors. In order to understand the sensing mechanism of specifically implanted samples, the change in the chemical structure of SiC at the surface and near the implant layers were analyzed using ESCA, micro Ramman, UV absorption spectroscopy and Raman techniques both before and immediately after exposure to hydrogen and Methane. The location of the implanted species was simulated using TRIM code as well as using RBS techniques. We will report the correlation of this simulation to the experimental results obtained from measurements of electrical properties, optical properties and surface analysis Research sponsored by the NASA Grant No. NG3-2302, and partially by the Center for Irradiation of Materials of Alabama A&M University and the Division of Materials Sciences, U.S. Dept. of Energy, under contract DE-AC05-96OR22464 with Lockheed Martin Energy Research Corp.

MM-WeP3 Polymer Based Microsensors Using Piezoresistive Microcantilever Technology*, **T.L. Porter**, M.P. Eastman, D. Pace, M. Bradley,* Northern Arizona University

We have tested a new type of microsensor based on piezoresistive microcantilever technology. In these devices, tiny beads of polymeric or functionalized polymeric material deposited on a substrate are in direct contact with the microcantilevers. Upon exposure to analytes, the polymers may expand or contract, and this volume change is measured directly by the piezoresistive cantilever. The measured response is a simple change in the resistance of the cantilever. There are many advantages of this type of sensor over microsensors based on chemiresistor or vibrating cantilever methods. Many individual sensing units may be incorporated into a "single chip" array using existing semiconductor fabrication techniques. Control and sensing electronics are very simple and inexpensive, making portable sensing arrays practical. There is no need to coat, functionalize, or attach species to the cantilever. Using biologically active layers in place of the polymeric materials, bio-sensor arrays may also be produced. In this paper, the piezoresistive cantilever technology is tested using plymers such as PEVA in the prsence of analytes such as toluene, hexane, water vapor, ethanol and acetone.

Processing at the Nanoscale/NANO 6
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Poster Session

NS+NANO6-WeP1 Nanometer Atomic Layer Growth and Removal from Surfaces of Inorganic Single Crystals: Scanning Probe Microscope Studies Under Controlled Solutions*, **J.T. Dickinson**, R. Hariadi, S.C. Langford,* Washington State University

Using the tip of a Scanning Force Microscope in solutions with controlled ionic content, we combine the application of single asperity forces to aquous surfaces of inorganic single crystals. With appropriate combinations of reactivity and stress, we are able to locally remove or deposit crystalline material in atomic layers and dimensions of nanometers. We show for the first time that layer by layer crystal growth can be controlled mechanically in such a fashion that fills in micron-sized features a few atomic layers deep. The recrystallization is done under supersaturated solution conditions. Step edges are stimulated with low contact force scanning using a scanning force microscope (which is also used to image the changes in surface topography. We present recent results on single crystal brushite (CaHPO@sub4@.2H@sub2@O) where we find strong dependencies on solution chemistry, mechanical parameters (e.g., normal force), and step crystallography. A model for both material removal and deposition will be presented. These studies allow production of nanoscale structures and atomically flat surfaces under low temperature conditions.

NS+NANO6-WeP2 Attractive Mode Molecular Manipulation at Room Temperature*, M.J. Humphry, **P.H. Beton**, P. Moriarty,* University of Nottingham, UK

We have investigated the manipulation of C60 on Si(100)-2x1 using the tip of a scanning tunneling microscope (STM) operating ultra-high vacuum at room temperature. During repulsive manipulation the tip follows a quasi-periodic trajectory as the molecule is displaced through integer multiples of the surface lattice constant and the tip is partially retracted during the manipulation process. A clear voltage threshold and characteristic tip response for this mode of manipulation is established. In addition molecules are observed to move through a displacement of up to three lattice constants (1.1nm) towards the STM tip due to an attractive interaction. This effect is observed over a wide range of tunneling parameters and is related to 'streaking' in STM images in which molecules may be dragged across the Si surface. The mechanism for this behaviour will be discussed together with the potential for the controlled assembly of molecular nanostructures.

NS+NANO6-WeP3 Manipulation of Single Cu-TBPP Molecules by Low Temperature STM*, **F. Moresco**, G. Meyer, K.H. Rieder,* FU Berlin, Germany*; H. Tang, A. Gourdon, C. Joachim,* CEMES CNRS Toulouse, France

The development of integrated nanoelectronic devices and the requirement of assembling perfectly identical nanostructures has recently focused the research attention on the vast range of possibilities offered by molecular structures. Controlled positioning of individual molecules can be performed by lateral manipulation with the STM tip. STM is in this respect a very promising technique because it contemporarily allows to determine the structure and conformation of the molecules and to build controlled molecular nanostructures without affecting the internal structure of the molecules. A detailed investigation of the processes involved in the manipulation of individual porphyrin-based molecules by scanning tunneling microscopy at low temperature is presented. The molecular conformation on different Cu surfaces is discussed. We show that the molecules occupy different configurations, depending on the interaction with the substrate and on the orientation of the four lateral substituent groups. By means of vertical and lateral manipulation it has been possible to switch between the different conformations and to exploit in detail the interaction between the STM tip and the molecule. Due to the complicated structure of the molecules we have explored different manipulation techniques, exploiting not only constant current but also constant height lateral manipulation.

NS+NANO6-WeP4 Nanolithography on Silicon Surface using a Tuning-fork STM/AFM*, **S.Y. Lin**, S.C. Yang, J.-D. Su,* National Taiwan University*; D.P. Tsai,* National Taiwan University, Taiwan*; F.S.-S. Chien, S. Gwo,* National Tsing-Hua University, Taiwan*; W.-F. Hsieh,* National Chiao-Tung University, Taiwan

A tapping-mode atomic force microscope (AFM)/scanning tunneling microscope (STM) system using a non-optical tuning fork force-sensing method has been developed for the scanning probe lithography.

Comparing with the nano-lithography done by the AFM having the conductive cantilever tip, our method has the following advantages: (1) It has longer tapered length STM tip and smaller half cone angle to perform the nanometer scale patterning with high aspect ratio. (2) Its low cost tungsten or Pt/Ir STM tip can be easily fabricated and attached to our AFM force-sensing tuning fork. (3) It can be easily adapted to large-scale parallel processing because of the all-electric force-sensing method. Nanostructures with high aspect ratios and large depths have been successfully performed on the silicon surfaces by using our AFM/STM nano-patterning system followed by the differential etching process. Lines with different widths and matrix of dots with various diameters were demonstrated for potential applications.

NS+NANO6-WeP5 Etching of GaN (0001) with Halogens: Pit Growth and Step Etching by Cl*, **K.S. Nakayama**, S. Kuwano, Q.Z. Xue,* Tohoku University, Japan*; Q.K. Xue,* Chinese Academy of Science*; T. Sakurai,* Tohoku University, Japan

We have studied the etching of GaN (0001) by Cl using scanning tunneling microscopy (STM) to obtain morphological information that can be related to surface reaction and desorption pathway. We used N- and Ga- polar GaN surfaces prepared by N-plasma-assisted molecular beam epitaxy (MBE) followed by Ga deposition. A Ga rich GaN(0001) surface was exposed to molecular Cl@sub 2@ at room temperature for the coverage of more than 1 monolayer. Heating to 600-700 °C induced etching by thermal desorption. STM images show that smooth and rough steps appeared and these triangle pits were initiated on the terrace after the thermally activated reaction. The height profiles of a pit and a step in the STM images reveal layer-by-layer removal of GaN. The etching directions of steps can be attributed to the number of dangling bond at the step edges. We also discuss possible desorption pathways with atomic scale including the formation of volatile GaClX products and the spontaneous desorption of nitrogen molecule. When the Ga atom on the top layer removed by Cl, the nitrogen atom in the second layer appeared having two dangling bonds. This configuration would be energetically unfavorable and the distance of dangling bonds of neighboring nitrogen atoms is very close. Therefore, the nitrogen atoms would combine each other to form nitrogen molecules and the spontaneous desorption would occur on the surface.

NS+NANO6-WeP6 Adsorption of Benzene and Pentacene on Metal Surface: A Scanning Tunneling Microscope Study*, J.-Y. Park, Y.-J. Song,* ***Y. Kuk****,* Seoul National University, Korea

A single benzene molecule is known to have three different shapes in scanning tunneling microscope(STM) image depending on the adsorption sites. The ordered benzene layer and the (3X3) benzene layer coadsorbed with carbon monoxide on Pd(111) are studied with STM. It is revealed that the ordered benzene layer can transform to the disordered layer with temperature or defects on substrates, suggesting the small heat of adsorption. The (3X3) benzene layer coadsorbed with carbon monoxide on Pd(111) is more stable than that without carbon monoxide. Unusual phase boundary was found at every other benzene rows, suggesting elastic strain in the layer. On the other hand, pentacene is known as a candidate for organic device. The adsorption and electronic structure of pentacene, adsorbed on Cu(111) surface, is also investigated with STM. The electronic and geometric contribution to STM image will be discussed with temperature dependent scanning tunneling spectroscopy data.

NS+NANO6-WeP7 Substrate-Directed Self-Assembly of Rigid Metallodendrimers*, **J.C. Poler**,* University of North Carolina, Charlotte

The subject of our research is the study of rigid dendrimer molecules, assembled on surfaces. Dendrimers are a class of molecule synthesized from repeating units such that the molecular topology is self-similar. A new class of geometrically rigid metallodendrimers has been synthesized recently by MacDonnell et al., and is enantiopure. These multinuclear molecules with Ru2+ centers are planar with D3 symmetry. We shall present AFM images of the self-assembled dendrimers on functionalized and patterned surfaces. Because these dendrimers are charged we can direct their self-assembly with electrostatic interactions at the surface. Theoretical, molecular mechanics and experimental support for this process will be described.

NS+NANO6-WeP8 Amino-Terminated Self-Assembled Monolayer on SiO@sub 2@ Surfaces Formed by Chemical Vapor Deposition*, **A. Hozumi**,* National Industrial Research Institute of Nagoya, Japan*; H. Sugimura,* Graduate School of Nagoya University, Japan*; Y. Yokogawa,* National Industrial Research Institute of Nagoya, Japan*; K. Hayashi,* Graduate School of Nagoya University, Japan*; T. Kameyama,* National Industrial Research Institute of Nagoya, Japan*; O. Takai,* Graduate School of Nagoya University, Japan

In order to immobilize polymers, neurons, DNA and proteins etc., amino-terminated self-assembled monolayers (SAMs) have been applied. Although chemisorption of aminosilanes at the solid/liquid interface were studied extensively, there have been few reports on preparing aminosilane SAMs from vapor phase. Here, we report on the formation of an amino-terminated SAM on SiO@sub 2@/Si sample substrates on the basis of chemical vapor deposition (CVD). Cleaned SiO@sub 2@/Si substrates were exposed to vapor of aminosilane, that is, N-(6-aminohexyl)-aminopropyltrimethoxysilane (AHAPS) diluted with dehydrate toluene. Following CVD, these samples were washed by a successive immersion in dehydrate ethanol, dehydrate toluene, NaOH (1mM) and HNO@sub 3@ (1mM). This washing process was repeated several cycles. Finally, they were rinsed with MilliQ water and then blown dry with a N@sub 2@ gas stream. We have investigated in detail chemical and electokinetic properties of this amino-terminated SAM. The SiO@sub 2@/Si surface after CVD became hydrophobic showing a water-contact angle of ca. Thickness of the AHAPS-SAM was ca. 1.3 - (±)0.1 nm as estimated by ellipsometry. This value is comparable to the theoretical molecular length of AHAPS, i.e., 1.4 nm. As confirmed by AFM, the surface was very smooth and homogeneous with its roughness being almost identical to that of the SiO@sub 2@/Si substrate. Zeta-potentials of the AHAPS-SAM covered SiO@sub 2@/Si substrate were measured as a function of pH by means of an electrophoretic light scattering spectrophotometer. The surface was charged positively below its isoelectric point of pH 7-8, since the amine groups are easily protonated. Furthermore, we demonstrated micropatterning of the AHAPS-SAM based on the photolithography using an excimer lamp radiating vacuum ultra violet light of 172 nm in wavelength.

NS+NANO6-WeP9 Formation of Ferroelectric Nano-domains using Scanning Force Microscopy for the Mass Storage System*, **H. Shin**,* Samsung Advanced Institute of Technology & CRI, Korea*; J.G. Shin, S. Hong, J.U. Jeon,* Samsung Advanced Institute of Technology, Korea*; J. Woo, K. No,* Korea Advanced Institute of Science and Technology

Applying voltage between the conductive tip in atomic force microscope (AFM) and Pb(Zr,Ti)O@sub 3@ (PZT) films can cause the switching of ferroelectric domains in nanometer scale. Ferroelectric domains (less than 100 nm in diameter) were induced and analyzed. Imaging of ferroelectric domains was achieved by piezoresponse of the PZT films in contact mode of AFM with lock-in amplifier. De-convolution of the first harmonic signal from the lock-in amplifier reveals the details of the formation of nano domains in ferroelectric thin film materials. Formation and imaging of ferroelectric domains in nano size can be applicable to develop the future mass storage system with miniaturization and integration of the AFM through MEMS technology. In this paper, relevant issues, i.e. bit (induced ferroelectric domains) size dependence on poling voltage, pulse width, and film's thickness and microstructure as well as retention characteristics of the induced bits are discussed. In detail, the bit size showed a log-linear dependence on the pulse width and a linear dependence on the pulse voltage. Using the calculation of electric field distribution the size of the induced bits under certain pulse voltage and width was estimated and confirmed by the experiments. As a result it is clear that the thinner films are beneficial to induce smaller and more stable bits under the same poling voltage and pulse width. In addition retention loss phenomena of the induced ferroelectric domains were observed and carefully investigated. The retention loss can be described by an extended exponential decay which implies a narrow distribution of the relaxation times of the domains. Characteristic relaxation time was largely dependent upon poling time, domain size as well as film's microstructures. Finally, an effective way to improve retention failure of the induced ferroelectric domains was proposed and confirmed by experiments.

NS+NANO6-WeP10 Nanostrands of Poly(carbamatepropylsiloxane) on SiO2 Observed with Atomic Force Microscopy*, **H. Celio**, H. Cabibil, J. Lozano, J.M. White,* University of Texas at Austin

Poly(organosiloxane) polymers have recently received considerable attention due to their potential use as dielectric materials in advanced microelectronic applications. Using atomic force microscopy (AFM) and various spectroscopic methods (XPS, IR, Raman, SIMS), we have investigated the formation of linear strands of poly(carbamatepropylsiloxane) polymer (CPS) of nanoscale dimensions supported on native silicon oxide of Si(100). The CPS nanostructures were fabricated by the hydrolysis of @gamma@-aminopropylethoxysilane (@gamma@-APS) in a basic aqueous solution containing 3 @gamma@-APS: 1 K+ and excess CO@sub 2@. The CPS is deposited on SiO@sub 2@ by a spincoating procedure. The CPS nanostrands have lengths greater than 1000 nm, heights between 2 to 3 nm and widths on the average of ~10 nm. These strands are stable under ambient conditions for weeks. The linear directionality of these structures is dependent on the following parameters: 1) K+ cations, 2) strong hydrogen bonding interactions between propyl-NHCOO- and -NH@sub 2@ groups. The former is responsible for the formation of linear Si-O-Si backbone and neutralization of the carbamate (NHCOO-) group, while the latter is responsible for the self-assembly of CPS strands.

NS+NANO6-WeP11 Solution Deposition and Surface Characterization of Supported Gold Clusters*, C.C. Chusuei*, *X. Lai, K.A. Davis, P.S. Bagus, D.W. Goodman, M.A. Omary, M.A. Rawashdeh-Omary,* Texas A&M University

Nanosized Au cluster agglomeration has been a long standing problem in the preparation of planar model catalyst systems. A novel Au/TiO@sub 2@ catalyst preparation method was investigated. Six-atom gold clusters (in the form of a Au@sub 6@(PPh@sub 3@)@sub 6@ colloidal suspension) was deposited onto a TiO@sub 2@(110) single crystal via CH@sub 2@Cl@sub 2@ solution. Scanning tunneling microscopy (STM) and spectroscopy (STS) revealed structures consistent with unagglomerated, single unit entities. Electron stimulated desorption (0.12 Coulombs/cm@sup 2@) was then performed. X-ray photoelectron spectroscopy, high resolution electron energy loss spectroscopy (HREELS) and STM showed evidence for removal of the triphenyl phosphine ligands. Band gap measurements from HREELS, STS and theoretical calculations suggest that metal/metal oxide support interactions affect the Au electronic structure.

NS+NANO6-WeP12 Optical and Structural Properties of Ball Milled Produced Small Si Particles Embedded into a Sol-Gel Matrix*, F.J. Espinoza-Beltrán*, *L.L. Díaz-Flores, J.M. Yañez-Limón,* CINVESTAV-IPN, México*; J. Morales-Hernández,* Programa de Posgrado de Ingeniería, UAQ, México*; A. Mendoza-Galván,* CINVESTAV-IPN, México*; J. González-Hernández,* CINVESTAV-IPN, México, Mexico

Nano and micrometric silicon particles have been introduced into SiO@sub 2@ matrix produced by the sol-gel method, using tetraethyl-orthosilicate. The small Si particles were produced by grinding 99.999 % pure silicon granular polyfine in a low energy ball mill. The milling process, for various periods of time, was carried out in air conditions. For that reason, the small particles consist of a Si core surrounded by a SiO@sub x@ cap layer. According to infrared and Raman measurements, the Si core contains molecular structures of the form Si@sub n@, where n is in the range of 6 to 7. >From the position of TO IR active mode the value of x is estimated to be around 1.7. The silicon oxide cap also shows a strong LO mode, normally not observed at normal incidence in the IR absorption of planar SiO@sub 2@ thin layers. An IR line at about 630 cm@super -1@, also indicates that during the milling process, some atomic hydrogen is attached to the silicon particles. Sol-gel layers, with various Si particle sizes and various particle densities were prepared. The structural and optical properties of the as-prepared and heat treated, in the range of 100 to 800°C, powder and film samples were studied. The photoluminescence emission and optical absorption of the Si particles are related with their size and concentration.

NS+NANO6-WeP13 Fabrication of a Si Nanosize Pillar Array using Modified He/Cl2 Plasma Etching Process*, J.W. Kim*, *M.Y. Jung, D.W. Kim, S.S. Choi,* Sun Moon University, Korea

We have studied the effect of He flow rate on the dry etching process of Si and SiO2 layers using chlorine-based plasma. Experiments were performed using reactive ion etching system in order to fabricate a nanosize Si structure. The ion damage on the etch mask during etching process would hinder deeper and controllable etch profile. Rather than Ar gas, a He feed gas with Chlorine etch gas was exploited in order to reduce the ion damage. We have examined various etching characteristics of the He/Cl2 plasma and applied to fabrication of a Si pillar arrays. In this study, the fabrication of the Si pillar array with 5 micrometer height was successfully fabricated with 500 nm thickness electron beam resist only. We also fabricated the 10 micrometer deep Si trench with this modified He/Cl2 reactive ion etching system.

NS+NANO6-WeP14 A Novel Low Temperature Synthesis Route for Silicon Nanowires*, S. Sharma*, *M. Sunkara,* University of Louisville*; E.C. Dickey,* University of Kentucky*; R. Miranda,* University of Louisville

In this paper, we present a novel synthesis route for growing silicon nanowires at temperatures lower than the temperatures required for traditional vapor-liquid-solid (VLS) approaches that employ transition metals as catalysts. In the present work, gallium, which has low melting temperature (~30 °C) and broad temperature range for the melt phase (30-2400 °C at 1 atm), was used as a catalytic media for the low-temperature synthesis of silicon nanowires. Growth of silicon fibers was observed when silicon substrates covered with a thin film of liquid gallium, were exposed to a mixture of nitrogen and hydrogen in a microwave-generated plasma. The resulting silicon wires ranged from several microns to less than ten (10) nanometers in diameter. The observed growth rates were on the order of 100 microns/hr. Results indicate that this technique is capable of producing oriented rods, whiskers and with reasonable size distribution. We will present results showing the crystallinity, composition, patternability, and role of gas phase composition, obtained when using this technique. The growth mechanism in this method is hypothesized to be similar to that in other VLS processes, i.e., rapid dissolution of silicon hydrides in gallium melt, which catalyzes subsequent precipitation of silicon in one dimension in the form of wires. We believe that this technique offers several advantages over the conventional VLS technique using silicon-gold eutectic for catalyzed growth. In this technique, there is no need to supply silicon through the gas phase. Secondly, this technique in principle can operate at very low temperatures (<400 °C) thus allowing easier integration with other processing techniques and materials involved in electronics and opto-electronic device fabrication. Nanometer scale one-dimensional silicon structures such as nanowires and nanowhiskers are expected to be critically important in the future mesoscopic electronic and optical device applications.

NS+NANO6-WeP15 Fabrication of a Nanosize Oxide Aperture Array Coated with Thin Metal Films*, J.W. Lee*, *J.W. Kim, M.Y. Jung, D.W. Kim, S.S. Choi,* Sun Moon University, Korea

There have been considerable interests about the fabrication of the nano-size hole due to the potential application of the near field optical sensor or liquid metal ionsource. The 2 micron size dot array was initially patterned. After formation of the V-groove shape by anisotropic etching, dry oxidation was followed. In this procedure, the orientation dependent oxide growth was performed to have an etch-mask for dry etching. The reactive ion etching by the inductively coupled plasma system was performed in order to etch 90 nm silicon dioxide layer at the bottom of the V-groove and to etch the Si at the bottom. The negative ion energy on the bottom substrater would enhance the anisotropic etching by the Cl2 gas. After etching, the remaining thickness of the oxide on the Si(111) surface was measured to be 130 nm by scanning electron microscopy. After bulk micromachining from the backside Si wafer, the etched oxide aperture will be coated with metal thin film in order to improve the light trasmittance efficiency.

NS+NANO6-WeP16 Resolution Enhancement in Kelvin Probe Force Microscopy*, R. Shikler*, *O. Kazael, Y. Rosenwaks,* Tel-Aviv University, Israel

Kelvin probe force microscopy (KPFM) has become in recent years a valuable tool for characterizing and analyzing semiconductor surface electronic properties with nanometer resolution. The Kelvin probe force microscope measures the semiconductor work function by nullifying the electrostatic force between a vibrating tip and the semiconductor surface. It is accepted that the finite tip size in scanning probe microscopy can have a profound effect on the obtained topography image. This phenomenon is enhanced in KPFM measurements because the electrostatic force is long range, hence introducing topographic artifacts into the contact potential difference image. We propose an algorithm that improves the lateral resolution and reduces the topographic artifacts of the contact potential image by taking into account the full tip shape and the semiconductor surface. By using the real tip shape and sample topography (obtained using conventional blind tip estimation and dilation algorithms), the true contact potential difference image can be deconvoluted. A comparison of measured and deconvoluted KPFM images is presented, and the limits of the method are discussed.

NS+NANO6-WeP17 Effect of Beam Parameters in Electron Beam Induced Deposition of Rhodium from a Carbon Free Precursor: A Systematic Study*, **F. Cicoira**, I. Utke, P. Hoffmann, B. Dwir, K. Leifer, E. Kapon, D. Laub, H.J. Mathieu,* Swiss Federal Institute of Technology Lausanne, Switzerland*; P. Doppelt,* Ecole Superieure de Physique et Chimie Industrielle, Switzerland

Electron-beam induced deposition (EBID) offers unique advantages over classical resist-based processes, like the capability of depositing in situ conducting or dielectric materials, high aspect ratio supertips, air-bridges and other three dimensional structures. In our deposition system, based on a Cambridge S100 SEM with a thermionic tungsten filament, EBID is obtained by decomposing with the focused electrons a metal precursor directed to the sample surface by an internal needle. Carbon-free precursors are used to improve the purity of the EBID metal containing deposits. The inorganic precursor [RhCl(PF@sub 3@)@sub 2@]@sub 2@ allowed the deposition of nanocrystalline Rh containing supertips and nanowires with diameters down to 200 nm. Auger Electron Spectroscopy (AES) measurements show that the Rh deposits contain up to 60% of Rh. The rest of the deposit consists in P, Cl, N and O; no carbon could be detected after removal of the contamination layer. These results are confirmed by TEM investigation, revealing that the deposits have a crystalline structure and are covered by an amorphous 10-20 nm thick shell. TEM images allow also the determination of the Rh cluster size, which depends on the beam parameters used to induce the deposition and show that crystalline lines and tips with high Rh content can be obtained even when low deposition currents (some pA) are applied. In this work, we present a systematic study of the effect of the beam parameters on the properties of the deposits. Different two and three-dimensional structures have been deposited from the same precursor varying the electron energy, the electron current and the scanning speed of the electron beam. The obtained deposits have been characterized by Auger Electron Spectroscopy and Transmission Electron Spectroscopy to determine the chemical composition and the nanostructure for every set of parameters.

Organic Films and Devices
Room Exhibit Hall C & D - Session OF-WeP

Poster Session

OF-WeP1 Electrical Properties of Polyvinylidene Fluoride Films Prepared by Physical Vapor Deposition Method*, **G.B. Park**,* Yuhan College, Korea*; M.Y. Chung, S.W. Lee, S.H. Park, D.C. Lee,* Inha University, Korea

Poly Vinylidene Fluoride thin films were prepared by using a physical vapor deposition and high electric field applying method. Thin films were studied with DSC, FT-IR, X-ray diffraction and electrical conduction measuring system. The melting point of PVDF thin film increases with increasing substrate temperature. It is identified by FT-IR that the crystalline phase of @alpha@ type PVDF is transformed to @beta@ type with increasing electric field applied during preparation. It is found that the crystallinity of PVDF thin films increases from 49.8% to 67% with increasing substrate temperature from 30 to 80. The absorption current of @alpha@ and @beta@ type PVDF increases with increasing the electric field applied under measurement and the current increment of @beta@ type is higher than that of @alpha@ type. The ion hopping distance, derived from a relation between current density and measuring temperature, increases from 51.5 Å to 153.5 Å with increasing temperature. >From above results, the conduction mechanism of PVDF thin film is estimated as ionic.

OF-WeP2 Transport Gap and Polarization Energy at Metals (Ag, Au) - Organic Molecular Semiconductor PTCDA Interfaces*, **W. Gao**, A. Kahn,* Princeton University

The complexity of localization and polarization in molecular solids demands experimental determination of more reliable energy diagrams for charge carrier injection and transport phenomena than just from optical measurements. We use inverse photoelectron spectroscopy (IPES) and ultraviolet photoelectron spectroscopy (UPS) to investigate unoccupied and occupied electronic states of PTCDA (3,4,9,10 - perylenetetracarboxylic dianhydride) deposited on Ag. The interface shows metal-to-organic charge transfer and formation of polaron states. The relative shifts of the vacuum level and molecular levels were analyzed in the context of interface dipole model, extended to account for the evolution of polarization energy. The comparison between the splitting of the highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO) measured via UPS and IPES, and the optical gap measured via absorption measurements leads to an estimate of exciton binding energy E@sub e-h@ to be large (0.6eV), in accordance with the highly correlated nature of this molecular solid. We also use scanning tunneling microscopy (STM) and spectroscopy (STS) for PTCDA deposited on Au(111), and find results consistent with the UPS/IPES results. Work is supported by the National Science Foundation (DMR-98-09483).

OF-WeP3 Controlled Doping of Polycrystalline and Amorphous Molecular Organic Layers: Physics and Device Prospects*, X. Zhou, B. Maennig, M. Pfeiffer, J. Blochwitz, **T. Fritz**, K. Leo,* TU Dresden, Institut fuer Angewandte Photophysik, Germany

Organic dyes with a conjugated electron system are currently investigated intensively for optoelectronic applications. In contrast to classical silicon technology, the materials used for both research and devices such as organic light-emitting diodes (OLED) are usually prepared in a nominally undoped form, leading to scattering of device parameters and higher operating voltages as compared to e.g. polymeric devices. Shifting the Fermi level towards the transport states by doping can reduce ohmic losses, ease carrier injection from contacts and increase the built-in potential of Schottky- or pn-junctions. We present here the results of a comprehensive study of controlled p-type doping of various polycrystalline and amorphous organic materials by the strong organic acceptor F4-TCNQ (tetrafluoro-tetracyano-quinodimethane). It turns out that doping is more efficient for the polycrystalline materials like the phthalocyanines where doping enhances the conductivity by up to eight orders of magnitude (10@super -2@ S/cm). Nevertheless, we could show for the first time that also amorphous phthalocyanine layers (deposited onto cooled substrates) and amorphous wide-gap materials can be doped, i.e. their conductivity increases and their Seebeck coefficient decreases indicating a shift of the Fermi level towards the hole transport state. Amorphous wide gap materials like TDATA or TPD are commonly used as hole transport materials in OLEDs because they form smooth and stable layers. We show here that controlled intentional doping of these layers strongly reduces the operating voltages of OLEDs.

OF-WeP4 Cascade-Like Hybrid Organic-CdS Quantum Particle Architectures Studied by the Attenuated Low Energy Photoelectron Spectroscopy*, **A. Samokhvalov**, M. Berfeld, M. Lahav, R. Naaman,* Weizmann Institute of Science, Israel*; E. Rabani,* Tel Aviv University, Israel

Hybrid organic/inorganic matrices containing CdS quantum particles (QP) arranged in periodic layers separated by bilayers of arachidic acid/thioarachidic acid were prepared by Langmuir-Blodgett deposition on gold substrate. Within each layer, the QP are of the same average size of about 2.5 or 5nm, and the layers are arranged in cascade-like pattern. Electronic properties of the structures above were studied by the Attenuated Low Energy Photoelectron Spectroscopy in which a "pump" laser excites QP and a "probe" laser ejects photoelectrons either from gold or from the QP. This spectroscopy provides detailed information on electronic states of the QP and shows that they depend on the specific organization of the QP within the matrix, as well as on the interaction of the QP with the underlaying gold substrate.

OF-WeP5 Photoemission Investigation of Metal/CuPc Interfaces*, **L. Yan**, Y. Gao,* University of Rochester*; M.G. Mason, C.W. Tang,* Eastman Kodak Company

Metal/organic interface play an important role in organic light emitting diodes (OLED), which has been a very active field in the past few years because of their scientific and commercial significance. Copper phthalocyanine (CuPc) has been found to improve the electron injection when it is inserted as a buffer layer between the metal cathode and Tris(8-hydroxyquinoline) aluminum (Alq@sub 3@), the mostly used light emitting material in OLED. It is intriguing that CuPc, traditionally used as a hole transport material in OLED, can enhance electron injection at the cathode. To address this question, we investigated the formation and the energy level alignment at the interface between metals and CuPc, using X-ray and ultraviolet photoelectron spectroscopy (XPS and UPS) simultaneously. We found that unlike many other organic materials, CuPc has two components in C1s, whose relative intensity varies as the interface formation progresses. This property provides a unique avenue to determine the charge transfer, dipole formation and energy level alignment at the interface.

OF-WeP6 Photoemission Investigation of Energy Level Alignment and Chemistry in Al/CsF/Alq@sub 3@ Interfaces*, L. Yan, Y. Gao,* University of Rochester*; **M.G. Mason**, C.W. Tang,* Eastman Kodak Company

Organic light emitting diode (OLED) have attract great attention in recent years since the discovery of Tris(8-hydroxyquinoline) aluminum (Alq@sub 3@) based devices. One surprising discovery is that certain kind of metal/salt complex such as Al/LiF forms excellent cathode for electron injection, which is comparable in device performance to those made from low work function metal such as Li and Ca. However, Li has very small X-ray photoelectron spectroscopy (XPS) cross section, making it hard to investigate any possible interface chemistry. We have investigated the interface formation and energy alignment between Al/CsF and Alq@sub 3@, using ultraviolet photoelectron spectroscopy (UPS) and XPS simultaneously. The experiment result indicates that charge transfer to Alq@sub 3@ had occurred at the Al/CsF/Alq@sub 3@ interface, similar to Al/LiF/Alq@sub 3@ interface. While there is no reaction is detectable by photoemission between Al and LiF, there are significant changes in core level spectra between Al and CsF. On the other hand, the energy level alignment for the two systems is strikingly similar, which is consistent to the device performance studies. Based on these observation and simplified thermodynamic calculation, possible decomposition is proposed at the Al/LiF(CsF)/Alq@sub 3@ interfaces.

OF-WeP7 Scanning Tunneling Microscopy and X-ray Photoelectron Spectroscopy of Metal(Au,Ag) Deposited Alkanethiol and Alkanedithiol Layers*, **T. Ohgi**, W.-L. Deng, D. Fujita, H. Nejoh,* National Research Institute for Metals, Japan

The self-assembled monolayers (SAMs) of thiol molecules on Au(111) substrates have been extensively studied because of their easy preparation and potential for many applications. For example, in nano-electronics studies, application of the SAMs as a tunneling barrier@footnote 1@ is one of the attractive candidates since it is very easy to obtain widely spread, densely packed, well ordered and atomicaly flat surface and moreover, the thickness of the SAMs can be easily and exactly controlled by changing the length of the molecules. Electrical property of SAMs has so far been investigated by using a metal/SAMs/metal heterostructure, and their structural analysis has been mainly carried out by XPS, UPS, and ISS.@footnote 2@ In the previous study,@footnote 3@ we reported that in the case of SAMs of thiol molecules (HS(CH@sub 2@)@sub n-1@CH@sub 3@: C@sub n@S), evaporated gold atoms penetrate through the SAMs. They cannot support metal overlayers, but monoatomic-height Au islands grow at the interface of the Au(111) substrate and SAMs. On the other hand, in the case of dithiol (HS(CH@sub 2@)@sub n@SH: C@sub n@S@sub 2@)layers, small Au particles are formed on them. In this paper, we show the result of Ag deposited octanethiol SAMs and alkanedithiol layers and discuss the difference from Au deposited ones. Ag atoms penetrate through both layers and do not form particles on them. The temporal change of Au particles/alkanedithiol/Au(111) structure were also studied. Sequential observation shows that particles penetrate through layers in weeks and form monatomic height islands under layers. @FootnoteText@ @footnote 1@ R. P. Andres, et. al., J. Vac. Sci. Technol. A14,(1996) 1178 @footnote 2@ D. R. Jung, et.al., J. Vac. Sci. Technol. A14,(1996) 1779 @footnote 3@ T. Ohgi, H. -Y. Sheng, H. Nejoh, Applied Surface Science 130-132, (1998) 919, T. Ohgi, H. -Y. Sheng, Z. -C. Dong, H. Nejoh, Surface Science 442, (1999) 277.

OF-WeP8 Wavelength- and Time-Dependent Two-Photon Photoemission Spectroscopy of the Dye Coated Silicon Surface*, A. Samokhvalov, **R. Naaman**,* Weizmann Institute of Science, Israel

Two dye molecules of similar structure, Rhodamine B and Sulforhodamine, were adsorbed on n- and p-doped silicon. The effect of photoexcitation of the adsorbed species on electronic properties of the surface of silicon was investigated applying the Wavelength- and Time-Dependent Two-Photon Photoemission Spectroscopy (WD-TPPE). It was found that the adsorption of Sulforhodamine, but not of Rhodamine B, causes a decrease in workfunction. For both dyes, the photoemission from the dye-covered silicon is reduced upon photoexcitation. The time-dependent recovery of the photoemission gets shorter for Sulforhodamine and longer for Rhodamine B, compared to the non-covered silicon. These observations are explained based on the electron donating properties of the molecules. In the case of Rhodamine B, photoexcitation of less than 10@super-4@ of the molecules on the surface was enough to affect the photoemission yield.

OF-WeP9 Structure and Molecular Recognition Ability of Thiolated-cyclodextrin Monolayer on Au(111) Surface*, **S. Yasuda**,* University of Tsukuba, Japan*; I. Suzuki,* Tohoku University, Japan*; K. Yase,* National Institute of Materials and Chemical Research, Japan*; J. Sumaoka, M. Komiyama,* University of Tokyo, Japan*; H. Shigekawa,* University of Tsukuba, Japan

Chemisorbed monolayers of thiols and disulfides on gold, so-called self-assembled monolayers (SAMs), have been studied to develop the novel interfacial systems. Since they easily form stable and highly packed monolayers, they are considered to have high potential to fabricate the micro-morphology of materials. From the point of view to develop a molecular recognition sensor using this technique, we analyzed structure and molecular recognition ability of the LP-@beta@-CyD (@beta@-cyclodextrin modified with lipoamide residue) monolayers formed on Au(111) surfaces, by using scanning tunneling microscopy (STM) and cyclic voltammetry (CV) measurement. The detailed adsorption process was completely different from that predicted from the macroscopic analyses. According to the macroscopic analysis, the growth process was explained by the Elovich model, which is based on the repulsive interaction between adsorbed molecules. However, many island structures were formed with the immersion time, indicating that the interaction between LP-@beta@-CyD molecules is attractive. Although the structure of the LP-@beta@-CyD molecules in the adsorbed layer was disorder, formation of the monolayer structure was clearly shown by STM. In order to examine the molecular recognition ability of the LP-@beta@-CyD/Au(111), we performed CV measurement using two electroactive makers; ferrocenecarboxylic acid (FCA) and hexacyanoferrate (HCF). FCA molecules can be included into @beta@-CyD cavity, but HCF molecules can not be. Therefore, if the monolayer structure is densely formed with the CyD cavity being perpendicular to the surface, the oxidation-reduction current is expected to be observed only for the case of the FCA molecules, which in fact was clearly shown by our experiment. These results indicate that the LP-@beta@-CyD/Au(111) structure has high potential as a novel molecular recognition sensor with its selective permeability. (http://dora.ims.tsukuba.ac.jp Appl. Phys. Lett., 76 (2000).)

OF-WeP10 Growth Modes of Vacuum Evaporated Pentacene on SiO2, MoS2 and Au Substrates*, **S. Zorba**, Q.T. Toan, N.J. Watkins, Y. Gao,* University of Rochester

Pentacene is one of the most widely used active material in organic thin-film transistors because of its remarkably high mobility. We studied the growth modes of vacuum evaporated pentacene on SiO2, MoS2 and Au substrates using Atomic Force Microscopy. Pentacene films were grown side by side on SiO2 and MoS2 substrates and separately on Au substrate by vacuum evaporation at room temperature with a deposition rate of 0.6 @Ao@/s. Pentacene films grow on SiO2 substrate in a layer by layer manner with full coverage at average thickness of 20 @Ao@ and have the highest degree of molecular ordering with large dendritic grains among the three materials. Films grown on MoS2 substrate reveal two different growth modes, ice-flake like growth and granular growth, both of which seem to compete with each other. On the other hand, films deposited on Au substrate show granular structure.

OF-WeP11 Analysis of the Surface Morphology of the Initial Growth Layers of p-quaterphenyl on NaCl (001)*, **E.J. Kintzel, Jr.**[1,2], E.A. Akhadov, T.W. Trelenberg, J.G. Skofronick, S.A. Safron, D.H. Van Winkle,* Florida State University*; F. Flaherty,* Valdosta State University*; D.-M. Smilgies,* European Synchrotron Radiation Facility

We have investigated the structural properties of the initial growth layers of p-quaterphenyl (p-4P) vapor deposited on NaCl (001) using Atomic Force Microscopy (AFM), Helium Atom Scattering (HAS), and X-Ray Grazing Incidence Diffraction (GID). The series of AFM studies provides evidence of needle-like accumulations of p-4P nucleating around surface defects, a striped-phase region with a lateral spacing of approximately 25 nm, and a region which displays a transition from lying to standing orientation of the molecules. HAS investigations at ~50K for films grown at 200K reveal many diffraction peaks which do not appear at the higher temperature. The helium diffraction pattern suggests the formation of randomly oriented micro-crystallites. Our GID studies indicate self-assembly of oriented crystallites in thin films. In thicker samples the diffraction becomes isotropic, like a powder pattern, indicating a random distribution of crystallite orientations.

OF-WeP12 Preparation of Stable Organic Layers Attached to Metals via a Double Bond*, **H. Oudghiri-Hassani**, M. Siaj, E.M. Zahidi, P.H. McBreen,* Laval University, Canada

New methods for preparing inorganic-organic interfaces lead to new types of functionalized surfaces. We describe a method to attach organic layers to a conducting solid via the formation of a carbon-metal double bond. The substrate is bulk molybdenum carbide, a material displaying metallic- like conductivity and ceramic-like hardness, as well as excellent catalytic activity. Early transition metal carbides are also of interest because they

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

[2] **NSTD Student Award Finalist**

may form natural electrical contacts to carbon nanotubes in molecular electronics applications. The organic layers were formed by dissociatively chemisorbing carbonyl compounds on the carbide surface. By suitable preparation of the surface, and careful coverage control, layers stable to 1000 K could be prepared. The stability, structure and reactivity of these unprecedently stable layers were evaluated using several surface spectroscopies.

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

PS-WeP1 Plasma Damage in Etching of SrBi@sub 2@Ta@sub 2@O@sub 9@ Thin Films Using Inductively Coupled Cl@sub 2@/Ar and Cl@sub 2@/N@sub 2@ Plasma*, **D.P. Kim**, Chungang University, Korea; W.J. Lee, B.G. Yu,* ETRI, Korea*; T.-H. Kim,* YIT, Korea*; C.-I. Kim,* Chungang University, Korea

In recent years, non-volatile ferroelectric random access memory (FRAM) has been attracted great attentoin for the applications with fast switching speed, low operating voltage, and high radiation hardness. FRAM comes to be used where high performance and power efficiency are required, in such as communication products, portable applications, logic IC, and smart cards. For highly density FRAM, one transistor and one capacitor structure (1-T/1-C) was proposed. Pb(Zr@sub 1-x@Ti@sub x@)O@sub 3@ (PZT), SrBi@sub 2@Ta@sub 2@O@sub 9@ (SBT) and Bi@sub 3.25@La@sub 0.75@Ti@sub 3@O@sub 12@ (BLT) have been challenged as dielectric materials of capacitor. Among them, SBT thin films have been attracted because SBT thin films show high dielectric constant, long data retention and fatigue endurance up to 10@super 11@ switching cycles. A few papers have been reported about etching mechanism and damages during SBT thin film etching. Therefore, SBT thin films were etched in Cl@sub 2@/Ar and Cl@sub 2@/N@sub 2@ plasmas by performing measurements of etch rates at different etching parameters such as gas mixing ratio, rf power, dc bias voltage, and chamber pressure. The chemical reactions on the etched surface were investigated with x-ray photoelectron spectroscopy and secondary ion mass spectrometry. Higher etch rate was obtained in Cl@sub 2@/Ar plasma rather than in Cl@sub 2@/N@sub 2@. Atomic force microscopy (AFM) was used to investigate the surface morphology of etched SBT thin films. High-resolution transmission electron microscopies (TEM) and auger electron spectroscopy (AES) were evaluated in order to investigate physical damages. Electrical properties were characterized by measuring leakage current. Physical damages were more severe at high bias voltage and in Cl@sub 2@/Ar plasma rather than in Cl@sub 2@/N@sub 2@. From the results, damages in etching of SBT thin films were due to ion bombardment. Low damages can be obtained at small ion mass and low bias voltage.

PS-WeP2 Design and Characterization of a Magnetic Pole Enhanced Inductively Coupled Plasma Source*, T. Meziani, P.P. Colpo,* ***F. Rossi****,* Joint Research Center, Italy

In the last decade, the ICs size shrinking has led to the development of a new generation of plasma source, enabling the generation of high plasma density with low ion energy: the Inductively Coupled Plasma sources (ICPs). ICP sources are widely used in semiconductor industry for their simple design, process flexibility and their high throughput. At present, the new challenge to be addressed is the scaling up of the plasma sources to enable large area specimen processing. Indeed, the semiconductor industry is now experiencing the transition from 200 to 300 mm wafer technology and plans the transition to 450 mm for 2010. On the other hand, the interest of the FPDs industry for larger area treatments is obvious for the flat video screen fabrication. The paper presents the design of a novel plasma source, enabling large area plasma treatment: the magnetic pole enhanced ICP (MaPE-ICP). The plasma source consists of a special arrangement comprising a special inductor embedded in a magnetic pole to create a concentrated and homogeneous magnetic field over large areas. We demonstrated that the plasma uniformity at laboratory scale (30cm) is better than the uniformity obtained with the classical ICP source on the same area. Furthermore, the obtained plasma characteristics (i.e. high densities of reactive species, low and controllable ion energy, wide pressure range) make the new source extremely promising for a whole range of processes such as large scale deposition, etching and plasma treatments. Finally, preliminary results of plasma density measurements over a large area MaPE-ICP reactor (1m x 1m) are presented.

PS-WeP3 Analysis of Chlorine-Containing Plasmas with Langmuir Probes, Self-Excited Electron Resonance Spectroscopy, and Optical Emission Spectroscopy*,* ***G. Franz****,* INFINEON Technologies, Germany*; P. Messerer,* Technical University, Germany

Capacitively coupled discharges of strongly reactive atmospheres, containing mixtures of boron trichloride and chlorine, are investigated employing spatially resolved Langmuir probe measurements, optical emission spectroscopy, and self-excited electron resonance spectroscopy. The analysis covers the whole area spanned by these gases from pure boron trichloride to pure chlorine, discharge pressure over more than one magnitude, and RF power half an order of magnitude. Their impact is addressed on important plasma parameters like plasma density, plasma potential, electron temperature, electron collision rate with neutrals, and actual RF power coupled into the discharge. Since the methods are partially complementary, a mutual control of the obtained data is made possible. Whereas the concordance in electron plasma density is surprisingly good, the discrepancies in the determination of the electron temperature lead to the conclusion that the electron energy distribution must be described with two temperatures. Compared to discharges of inert gases, which are used as calibration standard, electron plasma density and electron temperature are both definitely lower, which is mainly caused by electron attachment of the electronegative molecules. Absolutely no chlorine could be found in the plasma which is referred rather to the effective cooling of the Cl-containing species than to the nonexistence of these species.

PS-WeP4 Infrared Characterization of a Cascade Arc Plasma*,* ***R. Raghavan****, P. Morrison,* Case Western Reserve University

In-situ diagnostics of chemical vapor deposition (CVD) systems are limited in the mid-infrared (500-5000 cm@super-1@) region due to the lack of a high intensity light source. Noble gas cascade arc plasmas are potential high-intensity infrared light sources. We have constructed a argon cascade arc light source and characterized its infrared (2000-10000 cm@super-1@) emission properties using a Fourier transform infrared (FTIR) spectrometer. The properties of the plasma are adjusted by varying the pressure (1-4 atm) and the current (15-30 A) through the arc. To determine temperature from line emission of a plasma, the population distribution of excited states must be known. We show that our plasmas are in "partial local thermodynamic equilibrium" (PLTE) and use the Boltzmann equation to estimate excited state densities by assuming that only a fraction of the ground state Ar is in equilibrium with the excited states. This fraction as well as the plasma temperature are then regressed from a two-parameter least squares analysis of the measured infrared emission spectrum. Once we know the plasma temperature, we then estimate the electron density from continuum emission of the plasma. Alternately, we also estimate an electron density from the Saha equation. If the assumption of PLTE in our plasmas is valid, the electron densities resulting from these two techniques should be similar. Based on this observation, we find that the plasmas at the highest current (30 A) and pressures (3, 4 atm) satisfy the assumption of PLTE, while the plasmas at other conditions do not. This result enables us to calculate new transition probabilities for the infrared transitions in an Ar plasma. Plasma temperatures range between 9500-11500 K while electron densities are between 2-5x10@super22@ m@super-3@ for our plasmas. The total radiative power from the cascade arc is five times that of a conventional mid-IR light source like a globar and hence it is a feasible infrared light source.

PS-WeP5 Spatially Resolved Atomic Oxygen Concentration Measurements Using a Quartz Crystal Microbalance in a 300 mm Plasma Ash Chamber*,* ***A.K. Srivastava****, P. Sakthivel,* Eaton SEO

In a previous study, atomic oxygen (AO) concentrations have been measured in 200mm strip tools using a quartz crystal microbalance (QCM). This technique utilizes the resonant frequency of the crystals to monitor the mass gain of a silver film as it gets oxidized in an AO rich environment. Current work details similar results for high power plasma sources in a downstream 300mm dry strip tool. QCM data indicate that AO concentration is about 10@super 13@ per cubic centimeter under typical photoresist removal in 300mm systems. Data are presented on AO concentration sensitivity to varying process parameters like input gas mixture and chamber pressure. Additionally, correlation of AO concentration to photoresist strip rates on blanket-coated 300mm silicon wafers is made. Data indicate an increase in AO concentration as pressure drops, and a corresponding increase in resist removal rate. The effects on AO concentrations of using different showerhead configurations for uniformity in the chamber are also presented. By moving the QCM head within the chamber in the wafer plane, the spatial distribution of AO in the process chamber is mapped out. Finally, the use of an orifice on the QCM is shown to prevent overloading of the frequency counter, and a compensating transfer function may then be used to infer AO concentrations.

PS-WeP6 Plasma-Surface Diagnostics in LAPPS@footnote 1@*, S.G. Walton,* NRC Postdoctoral Research Associate*; D. Leonhardt, D.D. Blackwell, D.P. Murphy, R.F. Fernsler, R.A. Meger,* Naval Research Laboratory

In situ mass and energy resolved measurements of ion and neutral fluxes to a conducting electrode surface in NRL's Large Area Plasma Processing System (LAPPS) are presented. LAPPS uses a magnetically confined sheet of high-energy electrons to ionize a background gas, producing a high-density (10@super 9@-10@super 12@ cm@super -3@) planar plasma that is scalable to large areas (meters@super 2@). The electron beam is produced by a hollow cathode, embedded in a 100-300 Gauss magnetic field and injected into 20-200 mTorr of background gas. Hence, plasma production is decoupled from the reactor geometry, allowing independent positioning and biasing of electrode surfaces. The relative fluxes and energy distributions are reported for a grounded and rf-biased electrode and as a function of plasma-electrode separation. Ion and neutral species are sampled through a small orifice (sub-Debye length diameter) located in the center of the electrode and analyzed via an energy selector in series with a mass spectrometer. Relative fluxes and energy distributions are presented for discharges in Ar, O@sub 2@, Ne, and their mixtures over a range of conditions (pressure, mixture ratios). The results are discussed in terms of materials processing. Additional details concerning LAPPS and its processing applications are presented at this conference@footnote 2@. @FootnoteText@ @footnote 1@ Work supported by the Office of Naval Research. @footnote 2@ See presentations by co-authors at this conference.

PS-WeP7 Measurements of Plasma-wave Interactions in a Commercial-scale Helicon-driven Plasma Processing Reactor*, J.E. Norman,* *D.N. Ruzic, N. Li, M.E. Boaz, J.P. Allain,* University of Illinois, Urbana-Champaign

Measurements of plasma-wave interactions in a commercial-scale helicon-driven plasma processing reactor A Plasma Quest 256 research reactor powered by a PMT Mori 200 Helical plasma source has been used to study plasma wave interactions. Magnetically enhanced inductively coupled plasmas can operate in very different modes and operating regimes simply through external control. The ability to quickly change from one operating mode and plasma condition to another may allow the creation of multi-functioning processing environments: one machine that can replace many of the single-step chambers now required during semiconductor fabrication. To demonstrate this principle, Langmuir probe and spectroscopic measurements show that radically different plasmas can be produced through electrical and magnetic variation. Modeling has also been done which elucidates the physical mechanisms involved in the electromagnetic energy transfer to the plasma.

PS-WeP8 Spatial Profiles of Neutral, Ion and Etch Uniformity in a Large-Area High Density Plasma Reactor*, S. Yun,* *G.R. Tynan,* University of California, San Diego

The effect of ion and neutral uniformity on etch rate uniformity has been studied. In our experiments, the correlation between plasma conditions and etch uniformity has been measured in a large area high density plasma reactor. Spatial profiles of ion density, plasma potential, and radical density are measured across the face of a 20 cm wafer. Plasma profiles are measured by a Langmuir probe and radical density profiles are measured by an optical emission probe. Optical emission spectroscopy and spatial actinometry are used to calculate the spatial radical density on a wafer. As an initial experiment, we have performed the photo resist etching using oxygen plasmas. The results show that the spatial variation of etch rate is depend only on neutral profile when there is no applied substrate bias. The spatial variation of etch rate is depend on both neutral profile and ion flux profile when the bias voltage between -6 V and -100 V is applied on a substrate. The spatial variation of etch rate is depend on only ion flux profile when the bias voltage is below -100 V. These results are discussed including other effects such as spatial variation of wafer temperature. The results may suggest that ion uniformity may determine etch uniformity for processes which require significant energy sources from an energetic ion population (such as SiO@sub 2@ etching). Neutral reactant uniformity may determine etch uniformity for processes which do not require significant energy from ion energy (such as photoresist etching).

PS-WeP9 Probe Diagnostic Development for Electron-Beam Produced Plasmas*, D.D. Blackwell,* *S.G. Walton, D. Leonhardt, D.P. Murphy, R.F. Fernsler, W.E. Amatucci, R.A. Meger,* Naval Research Laboratory

The composition and distribution of particle species is the most basic in formation of a process plasma. Knowledge of the electron and ion energy distribution functions is prerequisite to obtaining accurate models of plasma surface interactions and radical production. NRL has developed a Large Area Plasma Processing System based on electron beam ionization of gases.@footnote 1@ The LAPPS plasma source, having low electron temperature and low pressure, make it ideal for probe diagnostics. However, such measurements can become difficult due to the presence of large magnetic fields, RF biases on the processing surface, high energy electrons, and multiple ion species. We have developed probe diagnostics with an emphasis on overcoming these difficulties. RF compensation methods for Langmuir probes and resolution of distribution functions on RF timescales with specially designed energy analyzers allow us to measure instantaneous and time averaged plasma proper- ties, while increased digital resolution allows for more realistic representation of non-Maxwellian distribution functions. Magnetic based current diagnostics give us instantaneous readings of to process surfaces and relation to RF biases applied. For calibration and fine tuning of probes for the LAPPS machine, a test chamber (75 cm wide x 25 cm high) with a spiral RF antenna coupled to the plasma through a glass window was used. Langmuir probes, temporally resolvable ion and electron energy analyzers, and capacitive probes were used to investigate the bulk plasma characteristics. Comparisons between the effectiveness of different probe diagnostics and correlations to other in situ diagnostics such as mass spectrometry,microwave transmission, and optical spectroscopy methods will be presented. @FootnoteText@ @footnote 1@ See presentations by co-authors at this conference.

PS-WeP10 Langmuir Probe Measurements in an Inductively Coupled Ar/CF@sub 4@ Plasmas*, M.V.V.S. Rao,* *M. Meyyappan, S.P. Sharma,* NASA-Ames Research Center

Technological advancement in the microelectronics industry requires an understanding of the physical and chemical processes occurring in plasmas of fluorocarbon gases, such as carbon tetrafluoride (CF@sub 4@) which is commonly used as an etchant, and their mixtures to optimize various operating parameters. In this paper we report data on electron number density (n@sub e@) temperature (T@sub e@) ion energy distribution function (EEDF), mean electron energy, ion number density (n@sub i@), and plasma potential (V@sub p@) measured by using Langmuir probe in an inductively coupled 13.56 MHz radio frequency plasmas generated in 50%Ar:50%CF@sub 4@ mixture in the GEC cell. The probe data were recorded at various radial positions providing radial profiles of these plasma parameters at 10-50 mTorr pressures and 200 W and 300 W of RF power. Present measurements indicate that the electron and ion number densities increase with increase in pressure and power. Whereas the plasma potential and electron temperature decrease with increase in pressure, and they weakly depend on RF power. The radial profiles exhibit that the electron and ion number densities and the plasma potential peak at the center of the plasma with an exponential fall away from it, while the electron temperature has a minimum at the center and it increases steadily towards the electrode edge. The EEDFs have a characteristic drop near the low energy end at all pressures and powers, and their shapes represent non-Maxwellian plasma and exhibit more like Druyvesteyn energy distribution.

PS-WeP11 Target Surface Modifications during Reactive Sputtering of Aluminium in an Argon-oxygen Plasma*, D.J.M.G. Depla,* *R. De Gryse,* University Ghent, Belgium

The target voltage of an aluminium target changes during magnetron sputtering when oxygen is added to the argon plasma. This target voltage alteration has been ascribed to a target surface modification, which alters the ion-induced secondary electron emission (ISEE) coefficient. As most models assume that the target surface modification is induced by chemisorption of oxygen on the aluminium target, we have measured the influence of chemisorption on the target voltage. At low oxygen exposure an absolute target voltage increase was noticed. Extending the oxidation period resulted in an absolute target voltage decrease. Comparing these results with the measurements performed regarding reactive sputtering, we came to the conclusion that chemisorption cannot explain the target surface modification during reactive sputtering. Indeed, stability experiments of the target surface modification induced by reactive sputtering clearly indicated that the target voltage gradually changes towards the value measured for a target fully oxidized by chemisorption. This shows that the target surface modification during reactive sputtering is not the formation of a stable surface compound by chemical reaction between oxygen molecules and the aluminium surface as noticed during chemisorption. The chemical reaction between implanted reactive gas atoms and the target atoms forms the basic idea of the presented approach to describe the target surface changes.

PS-WeP12 An Investigation of Plasma-polymer Interactions by Mass Spectrometry*, J. Hong*, *M.R. Wertheimer, L. Martinu,* Ecole Polytechnique Montreal, Canada

Modification of polymer surfaces by low pressure plasmas has gained industrial importance for controlling adhesion of coatings, wettability, printability and other surface-related properties. However, relatively little is known about the complex interactions of plasma with polymer surfaces. The present study is designed to investigate these interactions by mass spectrometry : in a special plasma reactor, which can be excited by microwave (MW, 2.45GHz), radiofrequency (RF, 13.56MHz), or dual (MW/RF) frequency power, polymer specimens are placed directly on the electrode, which also contains a small inlet-orifice (100 micron diameter) into the Hiden EQP 1000 plasma monitor/quadrupole mass spectrometer/ion energy analyzer. We observe molecular fragments from various polymers (polyethylene, polypropylene, polyethylene terephthalate, etc), which are liberated by chain scissions provoked by various energetic plasma constituents (ions, radicals, ultraviolet photons, etc). The different plasma modes mentioned above, and the choice of plasma gas (inert or molecular gases) allow us to select the dominant plasma species, their energies and fluxes during these surface treatments. Finally, we can study the desorption kinetics of species diffusing from beneath the polymer surface, which are created by UV irradiation.

PS-WeP13 Comparing Polyatomic Ions and Plasmas for Organosiloxane Film Growth from HMDSO*, E.R. Fuoco*, *L. Hanley,* University of Illinois at Chicago*; A.J. Beck,* The University of Sheffield, UK*; P.N. Brookes,* The University of Sheffield, UK, United Kingdom*; R.D. Short,* The University of Sheffield, UK

Mass spectrometric sampling has found that large polyatomic ions are formed during plasma polymerization of hexamethyldisiloxane (HMDSO), implying that these ions could contribute to polymerization at the surface. This study uses mass spectrometric sampling to detect these ions in a low power HMDSO plasma. Adjacent work employs mass-selected beams of 15 - 100 eV Si@sub 2@O(CH@sub 3@)@sub 5@@super +@ ions to deposit organosiloxane films on Al surfaces. Monochromatic x-ray photoelectron spectroscopy and time-of-flight secondary ion mass spectrometry are used to compare films formed from plasmas and those deposited from Si@sub 2@O(CH@sub 3@)@sub 5@@super +@ ion beams. These results support the argument that polyatomic ions and energetic neutrals play an important role in plasma polymerization.

PS-WeP14 Reactive Sputtering of Al@sub2@O@sub3@ in a Cylindrical Hollow Cathode Magnetron*, A. Pradhan*, *D. Guerin, S.I. Shah,* University of Delaware

Hollow Cathode Sputtering offers the advantage of 360-degree sputtering and allows the possibility to uniformly coat shaped articles, fibers and wires. We have studied the reactive deposition of Al@sub2@O@sub3@ using a hollow cathode sputtering process. A metal cylindrical target was used. Reactive sputtering process in a cylindrical magnetron is complicated due to redeposition of the sputtered flux. The control of the process is easier as it is relatively facile to pump to eliminate the unused reactive gas from a cylindrical magnetron than it is in the planar magnetron. We have characterized the reactive sputtering behavior of the Al metal target in Ar + O@sub2@ plasma. A hysterisis loop, typical of reactive sputtering, was obtained. The deposition rate, even in the poison mode, was high. This was perhaps due to the high pumping speed. The deposited film was also characterized by x-ray diffraction and x-ray photoelectron spectroscopy. The x-ray analyses revealed essentially pure metal films for low oxygen partial pressures. The pure metal to pure oxide transition, as the oxygen partial pressure in the sputtering gas was raised, was very slow. The transition region contained mixed valance aluminum. We will also present results on the optical and electrical characterization of the films.

PS-WeP15 High Rate and Low Damage Resist Ashing Employing Surfacewave Oxygen Plasma with High Permittivity Material Window*, H. Shindo*, *K. Kusaba,* Tokai University, Japan*; K. Shinagawa, M. Furukawa, K. Kawamura,* Canon Sales Corporation

Microwave plasma is one of candidates for large diameter plasma sources of the next generation. One issue in large diameter microwave plasma sources is on dielectric window material for microwave introduction. In this work, the microwave plasma production in a large diameter was studied employing a high permittivity window material. Especially, the plasma properties in O2 were examined in a viewpoint of the permittivity of the window material. If the microwave power is transferred into plasma in a surface wave mode, the plasma behaves depending on the permittivity of the window material. The plasma was produced in an aluminum chamber of 240 mm in diameter by introducing 2.45GHz microwave through a dielectric window of disc plate of 240 mm in diameter. Two kinds of dielectric materials, the quartz and alumina, were employed in this experiment and their permittivities were, respectively, 3.86 (14.9 GHz) and 9.7 (10 GHz), where the frequency used for the permittivity measurement was given in the parenthesis. The plasma parameters were measured by Pt plane probe of 1 or 0.5 mm in diameter in O2 plasma. The ashing rate of the photo-resist (PFI-58) was also measured at the substrate temperature of 200°. The results showed that the higher permittivity alumina window yielded two times higher electron density than the other in the regime above the cutoff of the microwave. Since the modes observed by the magnetic probe was consistent with the dispersion, it was concluded that the plasma production is due to the surface wave. The resist ashing experiments, which was performed in 8 inch wafer, showed that the rate was 2 times higher with the alumina than the other. A wafer damage was analyzed by both DLTS and carrier life time measurement, and it was concluded that a choice of the high permittivity window material provided one novel method for a large diameter wafer ashing processes with a high rate and low damage.

PS-WeP16 Etch Issues for Trench First and Via First Dual Damascene*, D. Keil*, *E. Wagganer, B.H. Helmer,* Lam Research Corporation

Dual Damascene etch technology is emerging as a key enabler for advanced integration schemes. Chief among these is copper integration. However, Aluminum integration is also of great interest. Of the candidate methods for doing dual damascene, Trench First and Via First are the primary approaches typically considered. Several etch issues typically arise when implementing either of these approaches. The via first approach can lead to problems with either via veils or excessive faceting when the trench is etched. The trench first approach requires very high selectivity to the underlayer when it is desired to place vias both in and outside the trenches. In both cases, it is frequently desired to have no stop layer when etching the trench. This places stiff demands on etch uniformity, etch front control and sidewall profile angle control. Furthermore, after these structures are etched, one typically must open the underlayer layer (typically nitride) at via bottom without excessive perturbation to the structures already formed. The complexity of these issues makes it especially important to understand the etch mechanisms responsible for controlling these issues. A review of these issues is given and the current understanding of the relevant mechanisms are discussed.

PS-WeP17 Thermal Effects in Atomic-Order Nitridation of Si by a Nitrogen Plasma*, T. Seino*, *D. Muto, T. Matsuura, J. Murota,* Tohoku University, Japan

In atomic-order nitridation of Si(100) by a nitrogen plasma, thermal effects were investigated using an ultraclean ECR plasma apparatus. The Si substrate was cooled by being put on the suscepter which was cooled by liquid nitrogen with flowing He as a contact gas. Nitridation was performed at the N@sub 2@ pressure of 1.3-5.1Pa. In the initial stage of nitridation, the N atom concentration on the Si surface was normalized by the relative radical density and the nitridation with radicals proceeded according to Langmuir-type kinetics neglecting desorption. In this stage, the N atom concentration was almost the same in both the cases with and without cooling the Si surface. On the other hand, in the second stage where the nitridation of the deeper Si atoms below the surface was induced, the cooling caused suppression and saturation at nitridation. Therefore, without cooling Si surface, it is considered that the nitridation of the deeper atoms was enhanced by heating due to the ion incidence. The N atom concentration with cooling became higher at a lower pressure where the ion energy was high. Furthermore, in the cases of the Ar plasma exposure on Si in the same pressure as nitridation, it was found that the Ar atoms penetrate below Si surface and the Ar atom concentration becomes higher at a lower pressure. Therefore, the saturated N atom concentration may be determined by the ion energy. The exact Si surface temperature measurements in the nitrogen plasma are under investigation.

PS-WeP18 Ion Assisted Deposition of Silicon Nitride Films using Electron Cyclotron Resonance Plasma*, **K. Denamma Vargheese**, G. Mohan Rao,* Indian Institute of Science, India

Ion assisted deposition (IAD) is one of the most widely used techniques for the deposition of thin films. Electron cyclotron resonance (ECR) ion sources are ideal for ion assisted deposition due to high ionization efficiency even at low pressures. Silicon nitride films have been deposited by RF reactive sputtering with ion assistance from a ECR plasma. The ECR power was varied from 0 to 250 watts. The effect of ECR plasma on the growth of silicon nitride films has been shown to be systematic and is characterized by using FTIR spectroscopy and Atomic Force Microscopy. The surface roughness for the films deposited without ECR plasma was about 2 nm and reduced to about 0.7 nm for those deposited with 250 watts of ECR power. Optical band gap studies also confirmed the effect of ion bombardment. The optical band gap changed from 2.2eV to 4.9eV as the ECR power is increased, indicating higher reactivity in the presence of ECR plasma. The optical transmittance of the films deposited with ECR assistance was good in the visible region reaching a maximum of 0.925 which is close to that of fused silica substrate used. Good quality silicon nitride films with a band gap of 4.9 eV, refractive index of 1.92 and extinction coefficient of 4x10@super -4@ have been obtained with a ECR power of 150 watts (corresponding ion density of 1.5x10@super 10@ cm@super -3@ on the substrate) and the surface roughness was less than 0.7 nm. Composition analysis carried out using Auger Electron Spectroscopy, showed a Si/N ratio of 0.76 for the films deposited under optimum deposition conditions.

PS-WeP19 Structural Studies of Hyper-thin SiO@sub 2@ coatings on Polymers*, **G. Dennler**,* Ecole Polytechnique de Montreal, Canada*; A. Houdayer,* University of Montreal, Canada*; Y. Ségui,* Université Paul Sabatier, France*; M.R. Wertheimer,* Ecole Polytechnique of Montreal, Canada

Transparent inorganic oxide coatings on polymers are playing an increasingly important role in pharmaceutical, food and beverage packaging. Such coatings are being prepared by physical-or by chemical vacuum deposition methods. They possess barrier properties when they are thicker than a certain critical thickness, d@sub c@ ; for d < d@sub c@, the "Oxygen Transmission Rate" (OTR, in standard cm@super 3@/m@super 2@/day/bar) is roughly the same as that of the uncoated polymer. This fact is commonly attributed in the literature to a "nucleation" phase of the coating, during which it is thought to present an island-like structure. In order to verify this hypothesis, we have deposited hyper-thin SiO@sub 2@ coatings on various flexible polymeric substrates (PET, PI, PP) using plasma-enhanced chemical vapor deposition (PECVD). The film thicknesses investigated here, well below d@sub c@ (typically in the range 1-15 nm), were determined by Rutherford Backscattering Spectroscopy (RBS), which allows us to determine the surface concentration of silicon. This was found to be a linear function of the deposition time, t, for t @>=@ 1 second. These results are compared with those from other thickness mesurements, namely spectroscopic ellipsometry, X-ray fluorescence, and transmission electron microscopy. Then, combining reactive ion etching (RIE) in oxygen plasma, scanning electron- and optical microscopy, we have been able to characterize the structure of the coatings : even for d @<=@ 2 nm, no island structure has been observed ; instead, we found continuous coatings which contain large concentrations, n, of tiny pinhole defects (with typical radii in the range of tens of nanometers), where n increases with decreasing d. These assertions are confirmed by grazing angle (80 degrees) XPS, which shows that even for d = 2 nm, the polymer substrate cannot be detected.

PS-WeP20 Numerical Study of HBr/O@sub 2@/CF@sub 4@ and HBr/O@sub 2@/CHF@sub 3@ Etching Chemistry in an Inductively Coupled Plasma Reactor*, **X. Xu**, P. Schoenborn,* LSI Logic Corporation

Inductively coupled plasmas (ICPs) have been developed for various applications in the modern integrated circuit manufacturing industry. One important ICP applicator for device fabrication is plasma etching of Si and other microelectronics materials because ICP reactors can produce high plasma density (10@super 11@ - 10@super 12@ cm@super -3@) at low pressure (a few to 10s mTorr). Increasingly stringent control of etching rates, profile shapes, and uniformity has led to using more complex chemistry mixtures in the selective etching of submicron features. There has been increasing interest in mixtures of HBr and fluorocarbons for etching of polysilicon and Si@sub 3@N@sub 4@ due to improved selectivity and superior control of the etched side wall profile. An understanding of the plasma chemistry is necessary and useful to examine plasma behavior from the source region to the substrate such as the fluxes of radicals and ions. In this study, we investigate the scaling of plasma chemistry mechanism of HBr/O@sub 2@/CF@sub 4@ and HBr/O@sub 2@/CHF@sub 3@ in an inductively coupled plasma reactor through a plasma simulation tool, the Hybrid Plasma Equipment Model (HPEM) developed at the University of Illinois. Addition of HBr into fluorocarbon plasmas cause significant reduction in F density. Results show that increasing gas pressure results in an enhanced Br flux and a diminished F flux in to the wafer. We will discuss the consequences of etching results of Si@sub 3@N@sub 4@.

PS-WeP21 Low-temperature Deposition of Thin Oxides for Si-LSIs Using Electron Cyclotron Resonance Sputtering*, **T. Ono**, K. Saito, Y. Taketa,* NTT Telecommunications Energy Laboratories, Japan*; S. Matsuo,* NTT AFTY Corporation, Japan

Electron Cyclotron Resonance (ECR) Sputtering has been investigated for application to Si-LSI processes of 8-inch wafers. The system consisted of the ECR sputtering process unit (with the ECR source coupled with divided microwaves),@footnote 1@ that was connected to an 8-inch wafer transfer system. For the deposition of aluminum oxides, the cylindrical sputtering target (Al: 99.99 %) was set around the plasma stream generated by ECR (gas: Ar/O@sub 2@). The sputtering was accomplished by biasing at 13.56 MHz rf utilizing ions in the plasma stream. The deposition was carried out without external heating; the wafer temperature during deposition was about 100 °C due to plasma heating. The film thickness ranged from 2 to 40nm. The uniformities of the deposited films were ±2.5 % (thickness), and ±0.3 % (optical refractive index of 1.61 at 632 nm) over a 200-mm-diameter. The resistivity and the brake-down strength of the 20-nm-thick films were about 5x10@super 14@ @OHM@cm, and 8 MV/cm, respectively. The dielectric constant was about 8. The fixed charge of the films depended on the oxygen partial pressure during deposition and can be controlled. ECR sputtering can be used for gate processes and capacitor processes at low temperature. @FootnoteText@ @footnote 1@ T. Ono et al., J. Vac. Sci. Technol. A12, 1281 (1994).

PS-WeP22 Silicon Etch Chamber and Process Development Using Diode Laser Measurements of HBr Concentration and Temperature*, **W. Collison**,* Lam Research Corp., U.S.A*; T. Ni,* Lam Research Corp.*; S. Chou, J. Jeffries,* Stanford University

Diode laser wavelength modulation spectroscopy technique developed by Stanford University@footnote 1@ has been used to measure HBr concentration and temperature in Lam 300mm TCP silicon etch chamber during blank poly silicon wafer etching. Various process conditions are measured. HBr concentrations as a function of pressure, gas flow, TCP power, bias power are recorded and correlated with etch rate data. HBr dissociation fractions are also measured before and after SF@sub 6@ waferless chamber clean with various focus ring materials including quartz, alumina, silicon nitride, silicon carbide. The results show that HBr dissociation fraction decreased 17% with the quartz focus ring after the chamber was cleaned by SF@sub 6@ plasma and about five wafers need to be processed before HBr signal gets to a steady level. Silicon carbide focus ring had essentially no influence on HBr concentration before and after chamber clean. Etch rate measurements show consistent results with HBr measurements. This suggests that using silicon carbide as focus ring material has certain advantages in poly silicon etch. It also shows that diode lasers can be used for real time control of plasma etch processes. @FootnoteText@ @footnote 1@ Shang-I Chou etc. "HBr concentration and temperature measurements in a plasma etch reactor using diode laser absorption spectroscopy", submitted to JVSTB.

PS-WeP23 Plasma Etching of Lead Germanate (PGO) Ferroelectric Thin Film*, **H. Ying**, J.S. Maa, T.K. Li, F. Zhang, S.T. Hsu,* Sharp Laboratories of America, Inc.

The lead germanate (PGO) thin film has been proposed for FRAM devices, especially for one transistor memory cell (1T) application. To realize such application, it is important to etch/pattern such thin film. In this work, plasma etching of PGO thin films was investigated by using chlorine or fluorine gas chemistries in an Electron Cyclotron Resonance (ECR) plasma reactor. Etch rates were studied as a function of etching conditions. The PGO etch rate of 600~650 Å/min was achieved by using a gas mixture of Cl@sub 2@ and Ar. In a pure Ar plasma, the PGO etch rate was significantly lower than that in a Cl@sub 2@/Ar plasma. The etching of silicon dioxide showed a similar trend under the same plasma conditions, however, the silicon oxide etch rate was much lower (~400 Å/min) than the PGO etch rate. In a CF@sub 4@/Ar plasma, the PGO etching behaves quite differently from the etching of silicon dioxide. While the silicon oxide etch rate increases with the CF@sub 4@ concentration, the PGO etch rate tapered off after the CF@sub 4@ concentration reached ~15%. In addition, similar to plasma etching of many other materials, the etch rate of PGO material increases as the RF bias power and/or the microwave power increases. The PGO etch rate decreases as the process pressure increases. Plasma etching induced damage to PGO thin film will also be discussed.

PS-WeP24 Morphological Study of a New Copper Dry Etching Process*, Y. Kuo,* ***S. Lee,*** Texas A&M University

Copper is the most desirable interconnect material for the high density VLSIC. Conventionally, it has been very difficult to etch copper using a parallel-plate plasma reactor under a mild condition, e.g., room temperature, low power density, etc., because reaction products, i.e., copper compounds, have low vapor pressures. Recently, the authors have published a new copper etching method based on a novel copper-plasma reaction.@footnote 1@ Instead of removing the reaction product during the plasma process, the copper film was consumed anisotropically and the copper compound was accumulated on the substrate surface. A solution was used to selectively dissolve the copper compound after the plasma process. The result shows that a high copper etch rate, e.g., > 3000 angstrom/min, could be achieved. The copper profile was adjustable with the plasma condition. In this paper, we are going to discuss the reaction mechanism of this new method under a large number of experimental conditions, such as feed gas, temperature, pressure, power, etc. The morphology change of the copper layer will be shown with SEM pictures. The physical and chemical analytical results of copper compounds will also be revealed. These results are critical to the understanding of this new copper dry etching process. @FootnoteText@ @footnote 1@Y. Kuo and S. Lee, Jpn. J. Appl. Phys. 39, L188-L190, 2000.

PS-WeP25 Titanium-Nitride Etch Techniques Using High Density Plasmas for Advanced BiCMOS/CMOS Applications*,* ***D. Galley,*** ATMEL Corp., Fab 5*; K. Sannes,* Applied Materials Corp., COS*; A. Kelkar, G. Frazier, M.J. Evans, M. Whiteman,* ATMEL Corp., Fab 5

The multitude of uses for Titanium-Nitride(TiN) have become evident as the integration of system-on-a-chip applications has forced the film to be used in a variety of ways. The conventional uses of TiN have been as a top anti-reflection coating and a W-plug glue layer. Given it's relative thickness(e.g. 250 - 600 A on 5-8 kA of Aluminum), the plasma etch characterization of the film has been limited to breakthrough etch techniques which focus on the impact of the process on the underlying film(i.e. the Aluminum). In this study, the new applications of TiN for (1) Spacer/Encapsulation Technology for Line-On-Line Vias, (2) TiN/Nitride/TiN/Aluminum Capacitors, and (3) Metal Etch Stop Layers show the dramatic challenges for plasma etch techniques as the TiN films/sandwiches can become >3500 A in thickness. In this study using an Applied Materials DPS reactor, the impact of plasma chemistry choice(e.g. Cl2/Ar, SF6/Ar, CF4/Ar, C2F6/Ar), cathode temperature choice(i.e. the impact of cathode temperature on grain boundary etching/surface roughness), source RF power configuration(e.g. ramp-on/no ramp-on), and the choice of bias RF power are shown to be critical to realizing the device specific requirements of the process. The impact of the ratio of Titanium to Nitrogen in the TiN film impacts the final process result, as well. The process deliverables are: the ability to etch TiN and stop on Al, the ability to etch TiN and stop on/in thin layers of PECVD Nitride/Oxide, and the ability to control profile of the thick TiN. The etch responses(for a given application) result in a variety of subsequent electrical parametric effects(e.g. Via Resistance, Floating Gate Threshold Voltages, Capacitor Sidewall Leakages) which will be reviewed. Therefore, the choice of plasma parameters and the success of implementation directly impacts the ability to produce the intended integration objective of employing TiN for a large variety of uses in system-on-a-chip applications. For each given application, a family of processes will be proposed.

PS-WeP26 Simulation of the Production of Atomic Hydrogen in a Low-pressure-arc-discharge-based Source*,* ***D.I. Proskurovsky,*** Institute of High Current Electronics, Russia*; V.A. Kagadei,* Research Institute of Semiconductor Devices, Russia*; A.V. Kozyrev,* Institute of High Current Electronics, Russia*; I.V. Osipov,* Tomsk University of Control Systems and Radioelectronics, Russia

Treatment of semiconductor and metallic materials in atomic hydrogen is a promising method used in microelectronic and nanoelectronic technologies for desired modification of their properties at the surface, at interfaces, and in the bulk. To produce atomic hydrogen, dissociation of hydrogen molecules in the plasma of a gas discharge is often used. A quantitative model has been proposed which describes the gas discharge and the processes responsible for the production of atomic hydrogen in a cylindrical cell of an atomic hydrogen source based on a low-pressure arc discharge. At the first stage of simulation the principal plasma parameters (the electron and ion densities, the currents of ions, fast electrons, and plasma electrons, and the currents of thermionic and secondary gamma-electrons) were calculated after which, based on the criterion for current self-sustaining, a calculation of the current-voltage characteristics (CVC's) of the discharge was performed. At the second stage the rate of production of atomic hydrogen was calculated for different parameters of the discharge. The following mechanisms for the generation of hydrogen atoms were considered: impact dissociation of molecules by fast electrons accelerated in the cathode fall region, dissociation of the discharge column plasma by thermal electrons, and dissociation at the surface of a hot cathode. The spatial distribution of the atomic hydrogen flux onto the end wall of the discharge cell has been calculated. The calculated CVC's describe adequately the experimental relations obtained for wide ranges of discharge currents and hydrogen flow rates. This has made it possible to refine some constants of unit processes, such as the coefficient of secondary ion-electron emission, the average energy going into the formation of an electron-ion pair, and the temperature of the hot cathode. The atomic hydrogen yield was estimated by the intensity of the luminescent emission from a luminophor and with the help of a sensor based on a thin-film resistor. Comparison of experimental and theoretical dependences of the atomic hydrogen yield on the discharge current, the gas flow rate, and the position of the extraction hole suggests that the proposed model describes adequately the process of production of atomic hydrogen.

PS-WeP27 Two-Dimensional Simulation of Pulsed Power Electronegative Plasmas*,* ***D.J. Economou,*** *B. Ramamurthi, V. Midha,* University of Houston

Low pressure electronegative plasmas are widely used for the fabrication of sub-micron semiconductor devices. Recently, pulsed power operation has emerged as a promising technique for reducing charge induced damage and etch profile distortion (e.g., notching) associated with conventional continuous wave discharges. This paper will report results of a 2-D fluid simulation of a pulsed-power inductively-coupled chlorine plasma. Simulation results show spontaneous separation of the plasma into an ion-ion core and an electron-ion periphery, depending on the negative ion to electron density ratio. The transition from an electron-dominated plasma to an ion-ion plasma in the afterglow was captured. The spatiotemporal evolution of the plasma for varying pressure, power, pulsing frequency and duty ratio has been studied. The evolution of negative ion density profiles is especially complex due to the formation of self-sharpening fronts during plasma "on" and subsequent back-propagation of the fronts during the plasma "off" stage of the pulse. Reactor geometry has a strong influence on negative ion evolution.

PS-WeP28 Kinetic Modeling of High-Density Diamond Deposition Plasma Chemistry*,* ***R. Blumenthal,*** Auburn University, usa

The chemistry of electron cyclotron resonance (ECR) microwave plasmas capable of diamond film deposition has been modeled using only neutral molecule energetics under the assumption that the plasma serves only as a constant source of hydrogen atoms. Supersonic pulse, plasma sampling mass spectra of 2% ethane in hydrogen and deutrium, 2% ethylene in hydrogen and deuteruium, 2% acetylene in hydrogen and deuterium and 4% methane in hydrogen and deuterium plasmas all have been fit with a single set of four physically realistic plasma conditions that were the only variable parameters in the modeling. The results of the calculations indicate that the primary reactive chemistry of C@sub 2@H@sub X@ species is the stripping of hydrogen from the hydrocarbons to produce acetylene, C@sub 2@H@sub 2@, which then undergoes closed-cycles of H(D) atom addition and abstraction for the balance of the species's lifetime in the plasma. The abstraction is the result of two-body collisions of the hydrocarbon with H(D) atoms generated by the plasma, while the addition is by a three-body collision, which is not observed (either experimentally or in modeling) for species other than acetylene. The notable exception is the ethane radical, C@sub 2@H@sub 5@, which in addition to the stripping chemistry, may react with H(D) atoms in a two-body collision to produce two methyl radicals, CH@sub 3@. Recombination of the methyl radicals is found to occur through the three-body reaction that produces ethane, C@sub 2@H@sub 6@. In deuterium plasmas, the resulting ethane is isotopically labeled and is responsible for the deuterated ethylenes observed only in the ethane and methane plasmas.

PS-WeP29 Evaluation of the Spatial Density of Sputtered Particles with Monte Carlo Simulation*, T. Nakano, S. Baba,* Seikei University, Japan

We have developed a method to evaluate the spatial density of sputtered particles in the sputtering process using Monte Carlo simulation. With the simulation, the elapsed time T@sub p@ of the particles (~10@super 5@ of trials) staying in a certain spatial region is summed up. In the same simulation, the time T@sub s@ required to emit all the trial particles is also calculated, by comparing the simulated arrival number of particles at the substrate with the deposition rate in the actual experiment. The number of particles in the spatial region can be obtained by taking the ratio T@sub p@/T@sub s@, and the spatial density is calculated by dividing it with the volume of the region. For the accurate calculation of T@sub p@, we have applied the model of the particle transfer in the gas atoms of Maxwellian distribution, which has been used successfully for the high pressure sputtering.@footnote 1@ In the present report, the calculated spatial density of the sputtered Cu is applied to explain the intensity of the optical emission from Cu in the plasma, because we have observed a different behavior in the pressure dependence between the emission at 324.8 nm and the emission at 510.6 nm in our previous report@footnote 2@. For gas pressures of 2~20 Pa and the deposition rate of 0.1~0.2 nm/s, the spatial density of the Cu atoms is found to be 10@super 17@~10@super 19@ m@super -3@ near the target. The density increases with the increase of the Ar pressure. This high spatial density of Cu atoms results in the self-absorption of 324.8 emission by those atoms at the ground state, which makes the increase of 324.8 line less steeper than the 510.6 line at higher pressures. @FootnoteText@ @footnote 1@ T. Nakano, I. Mori and S. Baba, Appl. Surf. Sci. 113/114 pp.642 (1997) @footnote 2@ T. Nakano and S. Baba, Vacuum in press.

PS-WeP30 An Analytical Solution to a Langmuir- Hinshelwood Surface Model of Si Dry Etching*, K.R. Milkove,* IBM T.J. Watson Research Center

This talk describes a Langmuir- Hinshelwood phenomenological surface model for the etching of a Si wafer in a low pressure, high density SF@sub 6@ discharge. The model yields an analytical solution, and its methodology is applicable to any etch system in which the dominant etch component is ion-enhanced energy-driven. Such systems exhibit first-order adsorption kinetics. As such they are characterized by an etching rate that is linear with respect to the feed gas flow rate at low values and nearly independent of flow rate at high values. The key to this model is the derivation of an analytical expression for the surface coverage of the Si wafer by an incoming flux of neutral atomic F. It is shown that when the system pressure is controlled by a variable position throttle valve, the surface coverage is a dependent variable of the total pressure, the feed gas flow rate, the surface area of the Si wafer, the F on Si reaction rate constant (k@sub r@), the temperature of the F neutrals within the plasma discharge, the F mass, and the F to Si, S to Si , and Si to Si sticking coefficients. All of these variables are treated as being independent except k@sub r@, which is defined as a function of source power, bias power and the Si-Si bonding energy. Analytical expressions are derived for the Si etch rate, the particle residence time, the partial pressure of neutral atomic F, and the effective pumping speed. A major observation of this model is the realization that k@sub r@ can be determined by equating the partial derivative of the Si etch rate equation with respect to feed gas flow rate to the slope of the linear portion of the experimental Si etch rate versus feed gas flow rate data.

PS-WeP31 Plasma Measurements and Simulations of a New Hollow Cathode Magnetron Plasma Source for Ionized PVD of Cu Seed Layers*, D.B. Hayden, M. Ow, K.A. Ashtiani, K.F. Lai, K. Levy,* Novellus Systems, Inc.

A commercial Hollow Cathode Magnetron (HCM) plasma source is used for depositing ionized Physical Vapor Deposition (PVD) copper (Cu) seed layers onto 200 mm wafers. Langmuir probes, an ion energy analyzer, and a deposition rate monitor are used to characterize the HCM plasma. Spatial scans of the downstream plasma regime, including near the wafer surface, are taken to measure the plasma densities, temperatures, and fluxes. Ionization levels, which greatly affect step coverage and uniformity, are analyzed versus different magnetic field arrangements. It is shown that the magnetic field arrangement near the cup-shaped target opening significantly affects the electron confinement in the source; thus the ionization levels of both argon working gas and sputtered copper. Based on the findings, improvements in the HCM source will be discussed which result in the ability to precisely control the ionization levels in the source as well as the uniformity of the arriving ion flux at wafer level. These improvements yield a 10-50% improvement in the Cu seed step coverage and a 10x improvement in deposited Cu uniformity. Sheet resistance and film thickness uniformities of <1% are achieved across a 200mm wafer. In addition, bottom coverages of 25% and 50% are achieved in 0.25um, 5:1 aspect ratio vias and trenches respectively. The plasma characterization results will be presented and compared to simulations from the Hybrid Plasma Equipment Model (HPEM).

PS-WeP32 New Reactor for High-rate Deposition of Functional Coatings on Polymer Substrates*, P. Bulkin, A. Hofrichter, B. Drevillon,* LPICM, Ecole Polytechnique, France

Concept of Multi-Magnetron Electron Cyclotron Resonance (MMECR) reactor was developed for applications in high-rate low temperature deposition of SiO@sub 2@/SiO@sub X@/Si@sub 3@N@sub 4@ multilayer and gradient films onto large area polymer substrates, flat and bended. Whereas broadly used electron beam evaporation and magnetron spattering techniques well suited and extensively used for multiplayer coatings, CVD and PECVD in particular do have clear advantages for gradient films deposition. We present an efficient concept of plasma reactor and report on process parameters. Flexible coaxial cables deliver microwave power to 25 magnetron applicators wich contain rare-earth NdFeB permanent magnets. Gas injection arranged through two distribution grids, one for silane and one for other gases, respectively. In the current version the system provides uniformity of better than 2 per cent on area of 35 cm in diameter (with magnetron antennas arranged in 30x30 cm plane and facing substrate) for both silica and silicon nitride films. Maximal growth rate obtained without compromising the quality of material is up to 6 nm/sec for SiO@sub 2@ and 1 nm/sec for Si@sub 3@N@sub 4@. Films are found to be dense and have good adhesion to polycarbonate.

Semiconductors

Room Exhibit Hall C & D - Session SC+EL+SS-WeP

Poster Session

SC+EL+SS-WeP1 Selectivity in Attachment of a Model pi-conjugated Organic Molecule to a Group IV Semiconductor Surface: Styrene on Si(001)*, M.P. Schwartz,* University of Wisconsin, Madison*; M.D. Ellison,* Wittenberg University*; S.K. Coulter, R.J. Hamers,* University of Wisconsin, Madison

The bonding of styrene to the Si(001) surface has been investigated as a model system for understanding selectivity in the attachment of conjugated pi-electron systems to semiconductor surfaces. Scanning tunneling microscopy images show one primary bonding configuration, slightly off-center from the middle of a dimer row. Infrared spectra using isotopically-labeled styrene establish that attachment occurs in a highly selective way, bonding through the external vinyl group and leaving the aromatic ring almost completely unperturbed. The implications for the high degree of selectivity in understanding attachment of other conjugated pi-electron systems are discussed.

SC+EL+SS-WeP2 Ferrocene and Decamethylferrocene Adsorption and Decomposition on Ag(100) and Si(111)*, C.M. Woodbridge, D.L. Pugmire,* University of Nebraska, Lincoln*; N.M. Boag,* University of Salford*; M.A. Langell,* University of Nebraska, Lincoln

Although metallocenes show potential as Chemical Vapor Deposition (CVD) source molecules, there is comparatively little known about their interactions with oriented substrates. We have investigated the adsorption and decomposition of ferrocene (FeCp@sub 2@) and decamethylferrocene (FeCp@sub 2@*) on Ag(100) and Si(111) using High Resolution Electron Energy Loss Spectroscopy (HREELS), Temperature Programmed Desorption (TPD), and X-ray Photoelectron Spectroscopy (XPS). For weakly-interacting systems such as those which occur with Ag(100), both FeCp@sub 2@ and FeCp@sub 2@* are adsorbed molecularly at 130 K. Monolayers of both FeCp@sub 2@ and FeCp@sub 2@* are oriented such that their molecular axes are perpendicular to the plane of the Ag(100) substrate; monolayer desorption occurs at approximately 250 K for both metallocenes. While FeCp@sub 2@ desorption is clean, FeCp@sub 2@* shows significant amounts of metallocene dissociation competing with molecular desorption. The Si(111)/metallocene systems also show molecular adsorption at 130 K but are more reactive to thermal decomposition upon heating and decompose primarily through hydrogenation and ligand-metal dissociation mechanisms. Specific information about the orientation of the adsorbed species and decomposition intermediates will be discussed.

SC+EL+SS-WeP3 Lowering of Processing Temperature due to a High Pressure Deuterium Anneal for Improved CMOS Hot Carrier Reliability*, **J. Lee**, K. Cheng, K. Hess, J.W. Lyding,* University of Illinois, Urbana*; Y.K. Kim, Y.W. Kim, K.P. Suh,* Samsung Electronics Co., Ltd.

The deuterium (D) isotope effect has been found to be very effective in reducing hot carrier induced degradation in CMOS transistors of numerous technologies. The magnitude of lifetime improvement (10x to 100x) varies from one technology to the other, but it directly correlates with D incorporation at the gate SiO@sub 2@/Si interface. Secondary ion mass spectrometry (SIMS) depth profiling has been used to make this determination. We have recently implemented high pressure D annealing to enhance its incorporation at the interface. By increasing the D pressure, the concentration at the interface can be increased for a fixed annealing temperature. Consequently, lower temperatures and shorter anneal times can achieve equivalent transistor reliability. This promises to be a technologically significant result for future CMOS production which requires a much lower thermal budget process due to the introduction of advanced materials (e.g. low k dielectrics) and increased number of metal layers. This high pressure annealing technique has been applied to one of the most recent CMOS technologies from Samsung Electronics. For these short-channel (0.18 µm) and low operating voltage (1.5V) devices, the isotope effect is substantially enhanced (700x). Rather than being scaled away, deuterium reduction of hot electron damage appears more relevant in future generations of CMOS integrated circuits. In the current work, the annealing temperature has been lowered from 450@degree@C to 350@degree@C. Although the lifetime improvement is not as great, we do observe a significant lifetime improvement (300x) just from changes in pressure. More experiments are in progress to maximize the D incorporation at the low annealing temperature. In addition, SIMS depth profiles are being determined for devices that were sintered at different annealing conditions.

SC+EL+SS-WeP4 Investigation of the Penetration of Atomic Hydrogen from the Gas Phase into a SiO@sub 2@/GaAs System*, **V.A. Kagadei**,* Research Institute of Semiconductor Devices, Russia*; E.V. Nefedtsev,* Tomsk University of Control Systems and Radioelectronics, Russia*; D.I. Proskurovsky,* Institute of High Current Electronics, Russia

Introduction of hydrogen into near-surface layers of semiconductor materials (hydrogenation) substantially varies their properties. In some cases hydrogenation improves the electrophysical parameters of the material and allows one to create devices with improved characteristics, while in other cases the penetration of hydrogen into a solid accompanies a technological process and causes unwanted changes in the parameters of the material. Therefore, it appears urgent to investigate the penetration of hydrogen into a semiconductor material, and a better understanding of this process will make it possible to optimize the technology of hydrogenation. The hydrogenation of GaAs samples coated with thin (5 nm) SiO@sub 2@ film was investigated. Samples were treated in a flow consisting of a mixture of atomic and molecular hydrogen produced by a source whose operation is based on a reflected arc discharge with a hollow cathode and a self-heating element. The hydrogenation time was 5 - 30 min, the hydrogenation temperature was 150 - 300 C, and the hydrogen pressure was varied from 10@super -1@ - 10@super -3@ Pa. It has been established that an increase in discharge current results in an increase in the concentration of atomic hydrogen in the gas phase, N, and in a decrease in the number of atoms penetrating into samples, and this is in contradiction with the usual notions about the penetration of hydrogen atoms into a solid. The data obtained suggest that the amount of hydrogen penetrating into samples is more dependent on the probability of the penetration of hydrogen atoms into a solid body, F, rather than on N. It has been proposed that F decreases substantially with decreasing the energy of the hydrogen atoms arriving at the solid surface. The energy of the atoms emerging from the reflected-arc-discharge-based source is estimated to vary between 0.1 and 10 eV. It is determined by the operating voltage of the discharge and decreases with increasing discharge current. Another possible cause of the observed phenomena is the formation of a near-surface diffusion barrier constituted by immobile hydrogen molecules, which occupy interstitials and retard the diffusion of atoms. The contribution of each of the proposed mechanism is discussed.

SC+EL+SS-WeP5 a-SiC:H Thin Films Fabricated by the High Rate Deposition Method*, **B.G. Budaguan**, A.A. Sherchenkov,* Moscow Institute of Electronic Technology, Russia*; A.A. Berdnikov, V.D. Chernomordic,* Institute of Microelectronics of Russian Academy of Science*; A.A. Aivazov,* UniSil Corp.

The a-SiC:H alloys are considered to be a perspective wide band gap material for different optoelectronic utilization. For the commercial application it is necessary to increase the deposition rate. However the increase of the growth rate results in the increase of structural inhomogeneity and in the deterioration of electronic properties of amorphous layers. Recently we have shown that deposition rate of a-Si:H films with high electronic properties can be increased with using of low frequency (55 kHz) glow discharge. In this work we investigated the growth mechanism and microstructure of a-SiC:H thin films fabricated for the first time by this method. The a-SiC:H films were deposited at different methane content from 0 to 100%, substrate temperatures T@sub s@ from 160 to 320 °C, and different discharge regimes: continuous wave and square wave modulated (SQWM). It was shown that the increase of the deposition rate of a-SiC:H films (5.3-11.1 Å/s depending on the methane content in gas mixture) in comparison with the standard deposition technology (3 Å/s for 13.56 MHz PECVD) is caused by the close position of a-SiC:H precursors formation to the growth surface. The joint analysis with using of infrared/optical spectroscopy and atomic force microscopy measurements showed that a-SiC:H films has the island type microstructure where the clustering of C atoms occurs at the island surfaces in the form of C-H@sub n@ bonds. The increase of C-H@sub n@ configurations on islands surfaces at high C content facilitate the relaxation of rigid a-SiC:H network through formation of flexible sp@super 2@-sites. The incorporation of Si-C bonds in the interior of islands determines the optical bandgap while the clustering of CH@sub n@ and SiH at the islands surface leads to the formation of graphite-like microstructure. It was shown that the suppression of formation of graphite-like microstructure at low T@sub s@ and in SQWM plasma allows to fabricate device quality alloys.

SC+EL+SS-WeP6 Mechanism for and Site of the Dissociative Chemisorption of XeF@sub 2@ on Si(100)2x1 Below 1 ML of Fluorine Coverage*, **J.R. Holt**, R.C. Hefty, M.R. Tate, S.T. Ceyer,* Massachusetts Institute of Technology

Upon exposure of a clean Si(100)2x1 reconstructed surface to a beam of xenon difluoride incident with an average kinetic energy of 0.9 kcal/mol, the XeF@sub 2@ dissociatively chemisorbs by atom abstraction solely on the Si dangling bonds up to a fluorine coverage of one monolayer (ML) before it begins to react with the Si-Si lattice bonds. This conclusion is based on the observations of scattered XeF and the preservation of the 2x1 dimer row reconstruction at 1 ML fluorine coverage. The scattered XeF is detected by a line-of-sight and differentially pumped mass spectrometer while the order of the surface is monitored by He diffraction. A clean Si(100)2x1 surface is characterized by three primary features in a He diffraction spectrum: a specular feature due to the smoothness and general order of the surface, a half-order feature due to diffraction perpendicular to the dimer rows, and a first order feature due to diffraction parallel to the dimer rows. The presence of the half-order feature at a fluorine coverage of 1 ML provides evidence that even the Si-Si sigma dimer bonds are undisturbed, preserving the original dimer rows. The reaction exothermicity of approximately 230 kcal/mol does not destroy the surface order. Molecular fluorine has previously been observed to react with a clean Si(100)2x1 surface in a similar manner by atom abstraction, saturating the Si dangling bonds at a coverage of 1 ML. The 2x1 periodicity is maintained. However, after saturation of the dangling bonds, F@sub 2@ ceases reacting with the surface while XeF@sub 2@ continues to deposit fluorine on the surface by its reaction with the Si-Si sigma dimer bonds and the Si-Si lattice bonds. The surface order is destroyed as a result of the continued fluorine deposition and ultimately etching occurs by the formation of volatile SiF@sub 4@.

SC+EL+SS-WeP7 STM Investigations of the Initial Ad- and Desorption Sites of Molecular Hydrogen on Si(001)*, **M. Dürr**,* Philipps University Marburg, Germany*; A. Biedermann, Z. Hu,* Columbia University*; U. Höfer,* Philipps University Marburg, Germany*; T.F. Heinz,* Columbia University

Whereas the extremely small sticking coefficients for dissociative adsorption of H@sub 2@ on Si surfaces indicate a high, the almost thermal energy distribution of the desorbing H@sub 2@ molecules points to a low barrier in the reaction channel. Recent molecular beam experiments have shown that this apparent contradiction is in full accordance with the principle of detailed balance and can be understood in terms of phonon-assisted sticking.@footnote 1@ To shed light on the underlying microscopic mechanisms, we have adsorbed H@sub 2@ on Si(001) at temperatures below the onset of H diffusion and investigated the site distributions with scanning tunnelling micrcoscopy (STM). The STM images show configurations of 4 adsorbed H atoms indicating a two-step process with an inter-dimer rather than the commonly assumed intra-dimer adsorption path as the relevant initial step. In the inter-dimer path, H@sub

2@ interacts with two dangling-bonds on adjacent Si dimers and forms a transition state with relatively large lattice distortion. Single-shot laser-induced thermal desorption experiments from nearly perfect hydrogen monolayers reveal distributions of unsaturated dangling bonds which indicate that the reverse path is also active in desorption. The influence of coverage, minority reaction channels as well as the consequences of the results on the reaction kinetics will be discussed. @FootnoteText@ @footnote 1@ M. Dürr, M. B. Raschke, and U. Höfer, J. Chem. Phys. 111, 10411 (1999).

SC+EL+SS-WeP8 Photoemission Study on Initial Oxidation of Si(001) Surfaces with Supersonic O@sub 2@ Molecular Beams*, Y. Teraoka,* Japan Atomic Energy Research Institute, Japan*; A. Yoshigoe,* Japan Atomic Energy Research Institute

We made a new surface reaction analysis apparatus at a soft x-ray beamline (BL23SU) in the SPring-8 (Super Photon ring-8GeV) to study incident energy effects for reactant chemisorption on semiconductor surfaces. As the first step, initial oxidation of Si(001) with O@sub 2@ has been investigated because that is not only interesting for surface reaction analysis but also important as electronic device development. The maximum incident energy was 3 eV in calculation. The clean Si(001) surfaces were irradiated by the supersonic O@sub 2@ molecular beams with various incident energy to achieve saturated adsorption. The oxygen amount on the surface was evaluated by measuring O-1s photoemission intensity. The intensity depended on the incident energy and two thresholds of 1.0 eV and 2.6 eV were found. These values are very resemble to the predicted values of 0.8 eV and 2.4 eV from the first-principles calculation, showing potential energy barriers for dimer backbond oxidation and oxygen insertion between the second and the third layer. Si-2p photoemission spectra were obtained at room temperature and 873 K by using high resolution soft x-rays from the beamline. In the case of room temperature, the maximum silicon oxidation number increased with increasing the incident energy from Si@super 2+@ to Si@super 4+@. Whereas a peak corresponding to SiO@sub 2@ was minor even in the case of 2.9 eV at room temperature, the peak was apparent in 873 K cases. Thermal energy may drive oxygen migration to form the SiO@sub 2@ structure. Even at such high temperature, incident energy affected in sub-oxide peak composition. The sub-oxide peak for Si@super 3+@ was increased with increasing the incident energy and was dominant in the case of 2.9 eV whereas the peak for Si@super 2+@ was primary in the case of 0.6 eV. The variation may be resultant from the Si@super 3+@ increase due to oxidation of dimer and sub-surface silicon atoms depending on the incident energy.

SC+EL+SS-WeP9 The Effect of Time and Moisture on the Adhesion Bond between Silica Particle and Silicon Oxide Substrate*, J.W. Feng,* *A.A. Busnaina,* Clarkson University

Adhesion of silica particles to silicon wafers is a problem that affects semiconductor manufacturing processes. The particle adhesion forces are greatly affected by the environment such as humidity, temperature and adhesion induced stress between the particle and the wafer following the particle deposition. The adhesion forces considered in the process include van der Waals, capillary force, double layer force and hydrogen bonding. In this study, silica particles are deposited onto wet and dry thermal oxide silicon wafers, then the samples are aged in different relative humidity environments. Results show that the largest increase in contact area between silica particles and thermal oxide wafers occur when the particle is first deposited on wet surface then aged in relative humidity above 55%. Higher humidity, results in higher adhesion force and lower removal efficiency. Results also indicate that adhesion force increases by more than two order of magnitude after the aging process. This suggests that hydrogen and covalent bonds are responsible for the increase in the adhesion force especially in humid environments.

SC+EL+SS-WeP10 Influence of Growth Direction on Order-Disorder Transition in (GaAs)@sub (1-x)@(Ge)@sub 2x@ Semiconductors*, A.G. Rodriguez,* ***H. Navarro-Contreras,*** *M.A. Vidal,* University, Mexico

We provide direct evidence of the dependence on the growth direction of the critical concentration of IV atoms at the order-disorder transition in ternary metastable (III-V)-IV, zincblende-diamond semiconductor alloys. The excellent agreement between the experimental and model predicted critical concentrations is evidence that the atomic ordering in these alloys is ruled almost entirely by substrate geometry. We report the observation of the critical concentration dependence on substrate orientation in (GaAs)@sub (1-x)@(Ge@sub 2@)@sub x@ metastable alloys, epitaxially grown on (001), (111), (112) and (113) GaAs. A different long-range order parameter behavior with Ge concentration is obtained for each growth direction, 0.36, 0.96, 0.59, and 0.50 ± 0.03, respectively, numbers that compare well with results of a Montecarlo simulation of the growth, 0.33, 1.0, 0.64 and 0.54, respectively.

SC+EL+SS-WeP11 Surface Electronic Structure of p-type GaN(000-1)*, P. Ryan,* *Y.C. Chao, K.E. Smith,* Boston University

Our investigation sought to describe the surface electronic characteristics of MBE grown (Mg-doped) wurtzite p-GaN (0001'). Four surface bands were mapped within the surface Brillouin zone. The peaks have been removed by atomic hydrogen exposure and three of the peaks show pz orbital configuration, the fourth an s orbital. The most interesting peak is a highly dispersing surface state which sweeps from the bulk valence band into the forbidden bulk band gap, approaches the Fermi level then returns to the bulk valence band. We compare this state to previously predicted mid-gap surface states.

SC+EL+SS-WeP12 Ultrafast Dephasing of Coherent Phonons by Lattice Defects in n-GaAs*, M. Kitajima,* *M. Hase, K. Ishioka,* National Research Institute for Metals, Japan*; K. Ushida,* RIKEN, Japan

GaAs is a key material for ultrafast switching and THz radiation because the carrier lifetime of low-temperature grown (defective) GaAs is ultrafast (sub-picosecond). In doped GaAs, the plasmon and the LO phonon form coupled modes through Coulomb interactions, and the frequencies of the LO phonon-plasmon coupled (LOPC) modes depend on the carrier density. We report the effect of active lattice defects on dephasing of coherent LOPC modes in He-ion irradiated n-GaAs by using a femtosecond pump-probe technique. The time-domain oscillations of the coherent LOPC modes in He@super +@ irradiated n-GaAs have been precisely measured for the different ion doses. The samples used were n-type GaAs with carrier density of ndop= 1.4x10@super 18@cm@super -3@. In order to examine the effect of point defects, 5 keV He@super +@ were irradiated to n-GaAs samples at doses of 9.4x10@super 12@ and 3.0x10@super 14@ He@super +@/cm@super 2@ in a UHV chamber with base pressure of 3x10@super -9@ Torr. The light source was a mode-locked Ti:sapphire laser with a pulse width of 25 fs. The anisotropic reflectivity change revealed coherent oscillations which shows beating pattern for the as-grown n-GaAs. This beating pattern in the time-domain data is due to an existence of the strong LO mode and the L@sub -@ mode. The mode beating changed clearly as increasing the ion dose, and the pattern of the Lmode disappeared at doses higher than 3.0x10@super 13@ He@super +@/cm@super 2@. The results suggest that defect-induced carrier trapping dominate annihilation of the coherent coupled modes. In addition we will also discuss on an anormalous behavior of dephasing of the coherent LO-phonon.

SC+EL+SS-WeP13 High Density Plasma Via Hole Etching In SiC*, H. Cho,* Miryang National University, South Korea*; K.P. Lee, P. Leerungnawarat,* University of Florida*; S.N.G. Chu,* Lucent Technologies, Bell Laboratories*; F. Ren,* University of Florida*; C.-M. Zetterling,* Royal Institute of Technology (KTH), Sweden*; S.J. Pearton,* University of Florida

Through-wafer vias ~100µm deep were formed in 6H-SiC substrates by Inductively Coupled Plasma etching with SF@sub 6@/O@sub 2@ at rates up to 0.8 µm·min@super -1@ and employing Al masks. Selectivies of @>@40 in SiC over Al were achieved. Electrical (C-V, I-V) and chemical (AES) analysis techniques showed that the etching produced only minor changes in reverse breakdown voltage, Schottky barrier height and near-surface stoichiometry of the SiC and had high selectivity over common front side metallization. The SiC etch rate and etch yield were measured as a function of plasma composition along with the selectivity over Al. This process is attractive for power SiC transistors intended for high current, high temperature applications.

SC+EL+SS-WeP14 RHEED Study of Ion-beam Induced Carbonization for 3C-SiC Heteroepitaxial Growth on Si(100)*, N. Tsubouchi*, *A. Chayahara, A. Kinomura, Y. Horino,* Osaka National Research Institute, Japan

3C-SiC heteroepitaxial film formation on a Si substrate is a very important when we consider compatibility with the silicon fabrication technology. So far, it has been reported that a carbonization process as buffer layer formation using various film-growth methods is effective for the heteroepitaxial film growth of 3C-SiC on Si while the lattice mismatch between 3C-SiC and Si is as large as 20 %. These methods reported for this reaction process, however, require high-temperatures ranging 700--1000°C, causing serious problems of redistribution of dopants and crystal defects such as dislocations and stacking faults especially at the heterointerface. In addition, carbonization reaction between provided gases including carbon atoms and Si substrates also results in promotion of defect formation in the Si-SiC interface. For solving these problems, a newly process, that is, ion-beam induced carbonization process of Si(100) with mass-separated energetic carbon ion species (e.g., @super 12@C@super -@, @super 12@C@sub 2@@super -@, @super 12@C@super +@ ions) was tried and investigated by RHEED measurements. The kinetic energies of ions and substrate temperatures were in the range 20-1200 eV and 400-700 °C, respectively. Such energetic species have possibility to lower a growth temperature inducing a decrease in defects and dislocations at the SiC/Si interface, in comparison with conventional methods. We report on the SiC growth condition during the carbonization process, i.e., ion-beam energy and substrate temperature dependence together with structural information.

SC+EL+SS-WeP15 Auger Depth Profile Analysis: Process Window Definition of 0.2 micron Aluminum RIE Interconnections*, C. Dziobkowski,* *L. Clevenger,* IBM Corporation*; M. Honda,* Toshiba, Japan*; R. Ramachandran,* Infineon Technologies

For fabrication of devices with dimensions of less than 0.2 microns, processing requirements become more demanding. New design requirements for the 256 Mbit DRAM also have higher aspect ratios. Process temperature control becomes very important because of the effects of temperature on the RIE etch, theta-Al2Cu precipitate distribution and texture. Eventually, even the electrical properties are affected resulting in device shorts and open circuits. This paper gives a description of the methodology developed to provide Auger depth profile analysis to characterize the copper distribution in the AlCu metallurgy. Copper segregation at the Al/Ti interface also affects the RIE process etching window. The information obtained from the Auger depth profiles can be used to define a window for VLSI devices with these small dimensions.

SC+EL+SS-WeP16 Epitaxial Growth of Cubic SiC Thin Films on Silicon Using New Single Molecular Precursors by MOCVD*, J.-H. Boo,* *S.-B. Lee,* Sungkyunkwan University, Korea*; K.-W. Lee, Yunsoo Kim, K.-S. Yu, S.H. Yeon, I.N. Jung,* Korea Research Institute of Chemical Technology, Korea

Heteroepitaxial cubic SiC thin films have been deposited on silicon substrates at temperatures in the range of 750 - 1000 ° C using newly developed single molecular precursors by MOCVD method. Single-crystalline, crack-free stoichiometric cubic SiC films were successfully grown on both Si(001) and Si(111) substrates without surface carbonization at as low as temperature of 920 ° C with 1,3-disilabutane (DSB), H@sub 3@Si-CH@sub 2@-SiH@sub 2@-CH@sub 3@, as a liquid single source precursor which contains silicon and carbon in 1:1 ratio. Cubic SiC thin films highly oriented in the [001] direction were also obtained on Si(001) using either a liquid mixture of 1,3,5-trisilapentane (TSP), H@sub 3@Si-CH@sub 2@-SiH@sub 2@-CH@sub 2@-SiH@sub 3@, and 2,4,6-trisilaheptane (TSH) at 980 ° C or 2,6-dimethyl-2,4,6-trisilaheptane (DMTSH), H@sub 3@C-SiH(CH@sub 3@)-CH@sub 2@-SiH@sub 2@-CH@sub 2@-SiH(CH@sub 3@)-CH@sub 3@ at 950 ° C without carrier gas. These growth temperatures were much lower than conventional CVD growth temperatures, and this is the first report of cubic SiC film growth using the single molecular precursors of trisilaalkanes.

SC+EL+SS-WeP17 Optical and Contact Properties of Indium Tin Oxide on p-GaN*, D.W. Kim,* *Y.J. Sung, J.W. Bae, G.Y. Yeom,* Sungkyunkwan University, Korea*; H.S. Kim,* University of Strathclyde, Scotland

Because Gallium nitride(GaN) is an attractive material which has an wide direct band gap, GaN-based optoeletronic devices such as light emitting diodes(LEDs) and laser diodes(LDs) in blue and ultraviolet wavelength regions have been studied intensively and fabricated successfully. However, the contacts to GaN-based LEDs are currently made by depositing metal layers on the top of GaN-based LEDs, therefore, significant optical loss is inevitable. In this study, we applied multilayers containing transparent conducting oxide such as indium tin oxide(ITO) to p-GaN and the effect of the optically more transparent contacts to p-GaN on the electrical and optical properties were investigated. As substrates, Mg-doped p-GaN layers were used. ITO thin films were deposited on p-GaN at room temperature using an oxygen radical assisted electron beam evaporator system. To improve the contact properties to p-GaN, various ITO/very thin metal multi-layer contact systems were also attempted and their electrical, structural, and optical properties were investigated. A semiconductor parameter analyzer and a four point probe were used to measure contact and electrical properties of ITO and mutilayer films on p-GaN. X-ray diffractometry(XRD) and Auger electron spectroscopy(AES) were used to investigate the structural properties of the contact during the annealing process, and an optical spectrophotometer was used to investigate the optical properties. The deposited ITO thin films showed the optical transmittance above 80 % at 420 nm(blue) with the sheet resistance of 40 ohm/sq. With ITO contact to p-GaN alone, Schottky contacts were generally obtained. However, depending on the applied very thin metal inter-layer and followed annealing conditions, different electrical and contact properties, which could be applicable to GaN devices, were obtained.

SC+EL+SS-WeP18 Visible Emission from Electroluminescent Devices using an Amorphous AlN:Cu, Mn, and Cr Thin Film Phosphor*, M.L. Caldwell,* *V.I. Dimitrova, M.E. Kordesch, H.H. Richardson, P.G. Van Patten,* Ohio University

Electroluminescence (EL) studies of AlN:Cu, Mn, and Cr alternating-current thin-film electroluminescent (ACTFEL) devices were performed at 300 K. Thin films of Cu, Mn, and Cr doped AlN, ~ 200 nm thick, were grown on p-doped silicon (111) substrates using RF magnetron sputtering in a nitrogen atmosphere. A transparent layer utilizing indium tin oxide was employed as the top layer contact. A strong bluish-green emission from the AlN:Cu films was observed under reverse bias due to electron impact excitation of the Cu atoms. The emission spectrum consisted of one broad peak in the visible region of 475 nm. a strong red emission from the AlN:Mn films was observed also under reverse bias due to electron impact excitation of the Mn atoms. There were two sharp emission peaks in the visible region at 680 nm and 700 nm. Studies of incorporationg the Cr@super +3@ ion will be performed to try to overcome the charge compensation problem. Temperature-dependent cathodoluminscence (CL) and photoluminscence (PL) studies will be performed between 30 - 450 K to determine the relationship of them to the EL results and show the optimum conditions for device performance.

SC+EL+SS-WeP19 Organic Contamination Removal on Silicon Substrate by Low Temperature Remote Plasma*, H. Kang,* *H. Soh, H. Seo, Y.C. Kim,* Hanyang University, Korea*; H. Jeon,* Hanyang University, Korea, South Korea

Organic contamination on silicon substrate deteriorates the film adhesion and forms deleterious decomposition during heating process. Organic impurities absorbed on the Si substrate surface generally desorbes in the form of volatile compounds by radio frequency (RF) remote oxygen and hydrogen plasma at relatively low temperatures. In this study, organic contamination removal and Si substrate surface microroughness by RF remote oxygen and hydrogen plasma will be described. The remote plasma system and analysis systems were connected by ultrahigh vacuum transfer system to avoid recontamination such as carbon absorption in the air. Organic impurity were intentionally contaminated and removed by hydrogen and oxygen remote plasma system. Surface contamination concentration and bonding state changes were analyzed by Auger electron spectroscopy (AES) and x-ray photoelectron spectroscopy (XPS). Surface morphology and microroughness were observed by scanning tunneling microscope (STM) and atomic force microscope (AFM). After remote hydrogen and oxygen plasma cleaning, carbon impurity was significantly reduced below detection limit of AES and the Si-C peaks of XPS were not observed. The surface microroughness generally degraded with increasing plasma power and exposure time.

SC+EL+SS-WeP20 Studies of the Surface Morphology, Chemical and Structural Changes of Ion Bombarded Silicon Carbide*, P. McCarty,* University of Alabama, Huntsville*; C.I. Muntele, I. Muntele,* Alabama A&M University*; M.A. George,* University of Alabama, Huntsville*; D. Ila,* Alabama A&M University*; D.B. Poker, D.K. Hensley,* Oak Ridge National Laboratory

Silicon carbide is gaining increasing interest for high temperature/harsh environment applications including miniature integrated sensors. In the past few years, efforts have been made toward controlling the defects and impurification that occur during various growth and fabrication processes. This work is intended to analyze the surface damage that occurs during ion implantation of silicon carbide, and the evolution of these defects. In order to correlate the effects that surface damage has on the sensing properties of ion implantation based silicon carbide gas sensors we have characterized these sensors under various conditions. We present the results of our investigation of the morphological, electrical and spectroscopic characteristics of ion implanted silicon-face 6H-SiC. In this work we have used He, O, Pd, and Au at energies between 100 keV to 8 MeV at fluences between 1 x 1015/Cm2 to 3 x 1017/Cm2. The ion bombardments were performed at both room temperature (300oK) and at elevated temperature (773oK). Atomic force microscopy, surface potential measurements and electric field microscopy was performed before and after ion implantation, as well as after the post-implantation high temperature annealing. This study is correlated with results obtained using micro-Raman, FTIR and Rutherford Backscattering Spectrometry. @FootnoteText@ We would like to thank Dr. David Larkin, NASA Glenn Research Center. Research sponsored by the NASA Grant No. NG3-2302, and partially by the Center for Irradiation of Materials, Alabama A&M University and the Division of Materials Sciences, U.S. Dept. of Energy, at the Oak Ridge National Laboratory, managed by UT-Battelle, LLC, for the U. S. Department of Energy under contract DE-AC05-00OR22725

SC+EL+SS-WeP21 Gallium Oxide Deposition and Radical Oxidation on GaAs(001)-(2x4) Investigated with STM*, **S.I. Yi**, P. Kruse, M. Hale, A.C. Kummel,* University of California, San Diego

Growth of metal oxide on GaAs with a low interface defect density is necessary for development of GaAs based metal oxide semiconductor field effect transistor (MOSFET). Vapor deposition of gallium oxide on GaAs(001) is emerging as a viable method for this objective. Using STM, we have investigated deposition of gallium oxide on GaAs(001)-(2x4) during the initial period and oxidation of the surface by atomic oxygen. Deposition of gallium oxide results in an atomically abrupt interface with the GaAs(001)-(2x4) surface, without disrupting the (2x4) surface order. In contrast, oxidation of GaAs(001)-(2x4) by atomic oxygen results in disordering of the surface characterized by formation of undimerized As surface atoms with half filled dangling bonds and As@subGa@ antisites. The stark difference in these two methods of oxide preparation has a profound implication for development of GaAs based MOSFET devices.

SC+EL+SS-WeP22 Density Functional Theory Studies of Semiconductor Surfaces*, G.S. Hwang,* California Institute of Technology*; **C.B. Shin**,* Ajou University, South Korea

Density functional theory (DFT) simulations have been proven to be a reliable and tractable tool in condensed matter physics. Indeed, these simulations are now successfully used to treat not only simple ordered solids but also complex systems such as surfaces and point-like/extended defects. We present the results of our recent pseudopotential based DFT studies which included: (i) the dynamics and configurations of Si(100) and (ii) the adsorption of hydrogen molecules on the surface. It is now rather well known that dimers on Si(100) are alternatively buckled at the ground state. However, the details of their geometry and dynamics at room temperature are still an issue of controversy. Our studies illustrate a tied flipping behavior of two consecutive dimers: the buckling of adjacent outer dimers becomes stronger while two inner dimers switch their orientations. Contrary to popular speculation, in most cases, the dimers undergo thermal fluctuations between two unequal energy minima, thereby preserving the 2x anticorrelation of dimer buckling along a row even at room temperature. Based upon such understanding of the dynamical behaviors of Si(100) at finite temperature, we have looked into dissociative adsorption of H@sub 2@ on Si(100), which is still ambiguous. This study reveals that intradimer @pi@-bonding disruption caused by thermal induced dimer stretching is mainly responsible for the anomalously strong surface temperature dependence of H@sub 2@ adsorption on the clean Si(100) surface.

SC+EL+SS-WeP23 Investigation of Polycrystalline Silicon Grain Structure by Single Wafer Rapid Thermal Chemical Vapor Deposition (RTCVD)*, **H. Bu**, C. Hu, M. Bevan, L. Tsung,* Texas Instruments*; L. Luo,* Applied Materials

It is known that the grain structure in poly-Si gate electrode can directly affect dopant activation and gate electrode depletion (GED). It is highly desirable to control the grain size and orientation during processing for improved IC device yield and reliability. This paper demonstrates the capability of tuning and generating a specific poly-Si grain structure with a lamp based and a heater based single wafer rapid thermal chemical vapor deposition (RTCVD) reactor at reduced pressure regime. Nitrogen gas is used as the carrier gas. The deposition temperature is varied from 650°C to 700°C. The effect of the concentration of intentionally added hydrogen during deposition is examined. Films deposited at various process conditions are characterized by TEM and XRD analysis. The results show that poly-Si grain size and orientation are sensitive to the hydrogen concentration. With a carefully selected process temperature and hydrogen concentration combination, the RTCVD technique is able to engineer the poly-Si grain size and orientation. The effect on poly-Si grain structure on electrical parameters such as electrical oxide thickness (EOT) and gate electrode depletion (GED) will be discussed.

SC+EL+SS-WeP24 Buried Low-Temperature (T@sub s@ <500 °C) Lateral Epitaxial Overgrowth of Si on SiO@sub 2@ Using Solid-Metal-Mediated Epitaxy*, **T. LaFave Jr.**, N. Lakshminarayana, A. Faik, M.-A. Hasan,* University of North Carolina

Buried lateral epitaxial overgrowth of Si on thin SiO@sub 2@ layers (<100 nm) using a thick solid Al layer as growth mediator was demonstrated using a newly developed solid-metal-mediated molecular beam epitaxy (SMM-MBE) method. The experiments were carried out at growth temperatures T@sub s@ < 500 °C using electron beam evaporation for Si and thermal evaporation of Al from an effusion cell. Si(100) wafers were thermally oxidized and patterned to provide seed/oxide strips ranging from 2/2 to 50/500 microns. Each seed/oxide strip was repeated within an area of ~ 1.25x2.00 cm@super 2@ and all patterns were placed on the same wafer. The wafers were then thermally etched at T@sub s@ = 900 °C under UHV conditions to desorb the remnant native oxide from the seed areas followed by deposition of Al at room temperature. Si deposited on the resulting structure at T@sub s@ < 500 °C re-grew epitaxially at the buried Al/Si interface and growth was extended laterally over the oxide layer. Initial TEM results demonstrated lateral growth of single crystalline Si over the oxide layer. This SOI method described above is based on SMM-MBE. In SMM-MBE, silicon grows epitaxially at a buried Al/Si interface during thermal evaporation of Si. Si atoms diffuse through the Al overlayer to the interface where low-energy atomic Si sites act as sinks for the diffusing Si atoms. This process is fundamentally different from surfactant assisted growth in which a small concentration of a metal (typically a fraction of a monolayer) is used to enhance epitaxial growth. In SMM-MBE, the Al layer can be thousands of monolayers thick (solid). The new findings may lead to new silicon-on-oxide fabrication method. Also, it provides a procedure for combined metallization and heavy p-type doping, e.g. in MOS device structure. Applications of this method in device fabrication will be discussed.

SC+EL+SS-WeP25 Field-Assisted Metal-Induced Crystallization of Amorphous Silicon Films*, **A. Khakifirooz**, S.S. Mohajerzadeh, S. Haji,* University of Tehran, Iran

Recently, metal-induced crystallization has gained special attention for low-temperature fabrication of polysilicon thin-film transistors. Metal-induced lateral crystallization, has been successfully utilized for obtaining high-performance TFTs. Very large silicon grains, free of metal contamination, are formed as a result of this lateral growth, providing a high carrier mobility. However, the lateral growth rate is still low and very long time annealing is required for practical applications. It has been reported that applying an electric field may enhance the growth rate. We have also observed this effect and the obtained results will be reported. Amorphous silicon films with a thickness of 1000Å are deposited on 50µm thick glass substrates via e-beam deposition. A 1000Å thick passivation oxide layer is subsequently deposited with e-beam and windows are opened for metal pads. A 1000Å thick nickel film is then deposited and patterned using photolithography. Samples are annealed on a hot plate while a DC voltage up to 100 V is applied between the pads. Growth rate is monitored using optical microscopy. SEM, TEM, and XRD are also used to investigate the crystalline structure of the films. A 300 µm crystallization was observed in samples annealed at 400°C for 30 min. when a 100 V/cm field applied. This is much higher than the previously reported growth rates. This may be explained by the fact that we have applied the field directly to metal pads, allowing a considerable current to pass through the a-Si film. Three regions with different crystalline structure are clearly observed in the laterally crystallized area when a high voltage is applied. The mechanism behind these phenomena will be discussed. In addition to filed-enhanced diffusion of Ni atoms, which has been supposed to be responsible for enhanced growth rate, we study the role of energetic electrons. Effect of impurities on the growth kinetics will be also reported.

SC+EL+SS-WeP26 Medium Range Order in Amorphous Silicon Films as a Function of Low-Energy Particle Bombardment During Growth*, **J.E. Gerbi**, J.R. Abelson,* University of Illinois at Urbana-Champaign*; P.M. Voyles,* University of Illinois and NEC Research Institute*; M.M.J. Treacy,* NEC Research Institute*; J.M. Gibson,* Argonne National Laboratory

Medium range order (MRO) refers to atomic correlations on a length scale of 1-2 nm. The recently developed TEM fluctuation microscopy technique@footnote 1@ is directly sensitive to MRO, as opposed to diffraction-based methods which are notably insensitive. In this work, we quantitatively compare the MRO in nominally amorphous hydrogenated Si thin films grown by significantly different vapor phase methods: plasma enhanced CVD, hot-wire (HW) CVD, and reactive magnetron sputtering (RMS). All films show significant MRO in the as-deposited state; the MRO decreases upon light soaking or thermal annealing, indicating the existence of a metastable state in the starting material. We investigate the roles of various particle bombardments in producing MRO with the RMS and HW-CVD growth processes. In previous work, we showed that bombardment by ions or neutrals promotes the formation of nanocrystalline or polycrystalline Si, depending on hydrogen addition and substrate temperature. We compare the MRO of a-Si:H, a-Si:D, and a-Si grown by RMS under high argon ion flux with that of a-Si:H grown by HW-CVD, which involves essentially no particle bombardment. We discuss how these bombardments affect the "structure" of a-Si in terms of MRO, and explain how this structure evolves during growth using the model of a frustrated polycrystalline growth surface which yields a highly strained, fine-grained "paracrystalline" structure. Such a structure looks amorphous in conventional diffraction methods, but is topologically crystalline. By contrast, the model of a continuous random network structure, as usually assumed for amorphous films, does not fit the data for as-deposited material. @FootnoteText@ @footnote 1@ J.M. Gibson, et al. Appl. Phys. Letts. 73 3093 (1998).

SC+EL+SS-WeP27 Cluster Deposition Study by Molecular Dynamics Simulation: Al Cluster and Cu Cluster*, **J.-W. Kang**, K.-S. Choi, E.-S. Kang, K.-R. Byun, H.-J. Hwang,* Chung-Ang University, Korea

Ionized cluster beam deposition for semiconductor interconnection technology has attracted much attention as a promising method for growing high-quality films at low substrate temperature. Therefore, it is important to understand the interaction between energetic cluster and substrate. In this work, we investigated energetic copper and aluminum clusters deposition and cluster-surface interactions. In the work, we used copper and aluminum clusters with the face centered cubic structure, a classical molecular dynamics simulation, and the second-moment approximation of tight-binding scheme. We simulated cluster deposition and investigated the variations of substrate temperature and the number of disordered atom as a functions of time, energy, and cluster size. The maximum substrate temperatures after energetic cluster impact on surface had linear relationship with total cluster energy and energy per atom, but we could not find any specific relationship with time taken for substrate temperature to reach its maximum. In this work, the correlated collisions between atoms in the cluster played a very important role in the impact on substrate surface and the correlated collision effect was proportional to the cluster size and kinetic energy per atom. For each impact angle and energy, we calculated the average properties such as sputter yield, sticking probability, average reflection angle of the impact cluster, and average emission angle of the sputter products. The calculated properties were compared with that of single atom deposition.

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

SS-WeP2 Substrate-Dependent Interaction of Carbon Monoxide and Ammonia on Metal Carbide Surfaces*, S.S. Perry, **L.C. Fernández-Torres**, R.L. Guenard, O. El-bjeirami,* University of Houston*; S.V. Didziulis, P.P. Frantz,* The Aerospace Corporation

A study of the interaction of carbon monoxide (CO) and ammonia (NH@sub 3@) with titanium carbide (TiC) and vanadium carbide (VC) is presented. The interaction of CO and NH@sub 3@ with the (100) face of the single crystal carbides was studied over the temperature range of 100-400 K. The adsorption states of CO and NH@sub 3@ were probed with high resolution electron energy loss spectroscopy (HREELS) and photoelectron spectroscopy. The desorption of CO and NH@sub 3@ was followed with temperature programmed desorption (TPD). Together, these measurements indicate that both CO and NH@sub 3@ adsorb molecularly on TiC and VC. However, HREELS measurements show CO adsorbs more strongly on VC than on TiC, and NH@sub 3@ adsorbs similarly on TiC and VC. TPD supports these observations; CO has a higher desorption temperature on VC than on TiC while NH@sub 3@ has a similar desorption temperature from the two surfaces. Strong evidence of @pi@-backbonding for CO on VC is seen in the vibrational data, as well as in the core and valence level photoelectron spectra. This mechanism, which is not active on TiC, differentiates the interaction of CO with these two substrates. Similar interaction mechanisms and adsorption energies are observed for NH@sub 3@ on TiC and VC, where @pi@-backbonding would not be expected to play a role. These results are discussed in terms of the difference in electronic structure between the two metal carbides.

SS-WeP3 Effects of Film Morphology on the Electron Stimulated Desorption of O@super -@ from O@sub 2@ Deposited on Benzene*, A.D. Bass, **L. Parenteau**, L. Sanche,* University of Sherbrooke, Canada

Low energy electron impact techniques can be used to study thin molecular solids under ultra high vacuum (UHV) and have already provided valuable information on the electronic interactions underlying phenomena such as radiation damage to biological materials, dielectric aging and surface mediated photo-chemistry.@footnote 1@ Experiments measuring the electron stimulated desorption (ESD) of ionic and neutral fragments have been of considerable value, yet only recently have researchers considered how factors such as film porosity or morphology affect ESD measurements.@footnote 2,3@ In this article we investigate the effects of film phase and porosity on the ESD of O@super -@ from O@sub 2@ molecules deposited onto the surface of multilayer benzene. Benzene films deposited at temperatures below 30 K are amorphous@footnote 4@ and appear porous so that O@sub 2@ molecules diffuse into their surface. When benzene is deposited at temperatures near 100 K, a non-porous film is formed which severely limits the penetration of O@sub 2@ into the benzene layer. The results are compared with measurements of O@super -@ production from O@sub 2@ covered water ices.@footnote 5@ @FootnoteText@ @footnote 1@See for example L. Sanche, IEEE Trans. Dielec. Elec. Insulat. 4, 507 (1997) @footnote 2@ W.C. Simpson M.T. Sieger T.M. Orlando L. Parenteau K. Nagesha L. Sanche J. Chem. Phys., @footnote 3@ E. Vichnevetski, P. Cloutier, and L. Sanche, J. Chem. Phys. 110, 8112 (1999) @footnote 4@ P.Swiderek and H. Winterling Chem. Phys. 229, 295 (1998) @footnote 5@ R. Azria, Y. Le Coat, M. Lachgar, M. Tronc, L. Parenteau, L. Sanche, Surf. Sci. 436, L671 (1999).

SS-WeP4 Electron Transfer Reactions on Layered Transition Metal Sulfide Surfaces+*, **K. Park**,* Baylor University

Recent advances in high resolution X-ray photoemission spectroscopy (HRXPS) have enabled one to directly probe an electron transfer reaction between adsorbates and model catalyst surfaces. For example, on cesium adsorbed molybdenum disulfide surface it has been observed that deposition of submonolayer cesium onto the basal plane of clean MoS2 introduces a new electron density of states at 1.25 eV above the MoS2 valence band maximum (VBM). Combined density functional theory and angle-resolved HRXPS indicate that the new VB state originates mainly from the bottom of the MoS2 conduction band, mixed to a small extent with the Cs 6s orbital. It has been further demonstrated that the supra-valence electrons in MoS2 can be captured and reacted with electron acceptor molecules forming surface ionic species. On the other hand, the interface between Li and MoS2 exhibits a quite different behavior - a reductive reconstruction. In this talk, I will review recent findings from alkali metal adsorbed, layered transition metal sulfide surfaces and discuss the on-going effort to understand the underlying principle for the adsorbate-substrate interaction.

SS-WeP5 Alloy Formation at the Co-Al Interface for Thin Co Films Deposited on Al(100) and Al(110) at Room Temperature*, **R.J. Smith**, N.R. Shivaparan, M.A. Teter,* Montana State University

High-energy ion backscattering spectroscopy and channeling (HEIS), combined with x-ray photoelectron spectroscopy (XPS) and low energy electron diffraction (LEED) were used to characterize the evolution of the Co-Al interface for thin Co films deposited on Al(001) and Al(110) surfaces at room temperature. This interface is of particular interest because of the possible applications for tunneling magnetoresistive junctions and the associated fabrication processes such as oxidation of Al films deposited on magnetic thin films. For the Al(001) surface, measurements of the backscattered ion yields from Al and Co show that substrate Al atoms are continuously displaced for Co coverages up to about 3 ML as the interface alloy forms. Cobalt metal eventually covers the mixed interface. Based on XPS intensity analysis, we conclude that a CoAl-like phase forms at the interface. A very diffuse LEED pattern with large spots and high background was observed after a deposition of 7.6 ML of Co coverage. For the Al(110) surface, intermixing of Co and Al atoms was observed up to 5 ML of Co deposition, where Co metal begins to cover the surface. No LEED spots were observed for any Co coverage exceeding 0.2 ML on the Al(110) surface. A Volmer-Weber type growth model for these interfaces was used with the XPS intensity data to characterize the morphology of the interfaces in both cases. In neither case was Co diffusion into the bulk Al substrate observed at room temperature. These results are briefly compared with similar measurements for Ni and Fe films on Al surfaces. Work supported by NSF Grants DMR9409025 and DMR9710092.

SS-WeP6 Defect Structures on the Si(5 5 12)-2x1 Surface*, **A.S. Sun**, K.M. Jones, E.S. Bowman, A.A. Baski,* Virginia Commonwealth University

Scanning tunneling microscopy (STM) studies of the high-index Si(5 5 12)-2x1 reconstructed surface show that it forms a single domain of row-like structures. It has therefore been proposed as a viable template for metallic nanowire growth. In this work, we use STM to characterize two common surface defects that may influence its application as such a template. The most commonly observed surface defects are disruptions in the periodicity of the Si(5 5 12) unit cell. The Si(5 5 12) unit cell can be considered as a combination of one (7 7 17) and one (337) unit cell. In up to 20 percent of the (5 5 12) units, an extra or missing (337) subunit appears, resulting in a non-uniform surface periodicity. Because there is a dominance of either extra or missing (337) units on a given sample, sample preparation conditions appear to play an important role. Another type of defect observed on the Si(5 5 12) surface is the presence of adsorbed dimers. These dimers have a typical coverage of 10-15 percent, and exist as single dimers or in clusters up to ~10 dimers long. Statistics taken from STM data indicate that as the dimer cluster size increases, the number of clusters decreases exponentially. A Monte Carlo model of 1D clusters has been used to correlate the distribution of these dimer defects with their relative "hopping" probabilities on different surface sites.@footnote 1@ We find that single dimers have a strong preference to remain attached to the ends of existing clusters. A better understanding of both the adsorbed dimer and (337) unit cell defects should lead to a more controlled preparation of Si(5 5 12) as a growth template. @FootnoteText@ @footnote 1@ E. S. Bowman, M. F. Bishop, T. McMullen, and A. A. Baski, Cluster and Nanostructure Interfaces, edited by P. Jena (World Scientific, New York, 2000), p. 569-574, in press.

SS-WeP7 Growth of a Group-IV Metal on Si(5 5 12)*, **I. Samanta**, A.A. Baski,* Virginia Commonwealth University

Recently, we have used scanning tunneling microscopy (STM) to study the growth behavior of noble metals (Ag, Au) on the row-like Si(5 5 12) surface.@footnote 1@ In this study, we explore the different growth modes for a Group IV metal such as Sn, where we expect more intermixing of the tetravalent Sn and Si atoms. Our STM studies show that, unlike for the noble metals, Sn forms adsorbed dimers on the Si(5 5 12) surface at low coverage (< 0.5 ML) and moderate annealing temperatures (~450C). These dimers appear as bright protrusions in the trenches between Si rows, and in fact intermix with existing Si dimers on the surface. At higher coverages, Sn forms relatively large protrusions with a 4x periodicity along the underlying Si tetramer rows. Such strongly corrugated features have never been observed for the deposition of noble metals, indicating a significantly different growth behavior for this group-IV metal. As the coverage is increased (>1 ML), Sn creates a disordered surface with only remnants of the row-like surface morphology remaining. At higher annealing temperatures (700C+), however, the surface undergoes a large-scale rearrangement with sawtooth facets being formed. We are presently exploring the optimal conditions to produce such sawtooths, because such a corrugated surface provides yet another interesting template for growth. @FootnoteText@ @footnote 1@ K. M. Jones, K. M. Saoud, and A. A. Baski, Cluster and Nanostructure Interfaces, edited by P. Jena (World Scientific, New York, 2000), p. 49-54, in press.

SS-WeP8 Cyanogen Iodide Adsorption on Si(100)*, **N.F. Materer**, T. Watt,* Oklahoma State University

The adsorption of cyanogen iodide (ICN) on a silicon (100) surface is studied by X-ray photoelectron spectroscopy (XPS). At room temperature, ICN chemically adsorbs on the surface. The C 1s photoelectron peak indicates that the carbon nitrogen triple bond is intact. The triple bond remains until approximately 400C. Initial experiments suggest a sticking coefficient at room temperature of 0.1 for ICN. Experiments are in progress to quantitatively determine this number. In addition, thermal desorption measurements are proceeding to further complementing the XPS studies.

SS-WeP9 Effects of Al/Si(111) Surface Phases on the Wandering of the Single-Height Steps@footnote 1@*, **I. Lyubinetsky**, D.B. Dougherty, H.L. Richards, T.L. Einstein, E.D. Williams,* University of Maryland, College Park

The thermally-induced wandrering of single-height steps have been studied by STM on a vicinal Si(111) surface, miscut by 0.5° in the [2,-1,-1] direction, after aluminum deposition at elevated temperatures (500-700°C). From direct measurement of the step-correlation function, the step diffusivity, b@super2@/a, is shown to increase strongly as Al coverage @Theta@ in the surface phases increases: b@super2@/a ~ 0.4 Å for the a(7x7) phase (@Theta@ = 0.12 ML), ~ 1.5 Å for the (@sr@3x@sr@3) phase (@Theta@ = 0.3 ML), and ~ 4.6 Å for the @gamma@ phase, also referred to as the (9.4x9.4) phase, (@Theta@ = 0.68 ML), implying corresponding systematic decrease in the kink energy. An increase of the step diffusivity compared to a clean Si(111)-(7x7) surface has been observed even at the very initial stages of the a(7x7) reconstruction formation, at @Theta@ as low as 0.02 ML. For the least stable phase of (@sr@7x@sr@7) (@Theta@ = 0.43 ML), which coexists with the @gamma@ phase on the same terrace, the wandering of the phase boundaries between (@sr@7x@sr@7) and @gamma@ phases will also been discussed. @FootnoteText@ @footnote 1@Work supported by the UMD-NSF-MRSEC.

SS-WeP10 Oxide and Nitride Film Growth on Microfabricated Cantilevers by Pulsed Mode DC Magnetron Sputtering*, P. Cao, M.-S. Lim, S.S. Perry,* University of Houston*; **K.P. Wiederhold**, Y. Yamaguchi, E.J. Mitchell, D.C. Koeck, H.C. Galloway,* Southwest Texas State University

We have investigated the growth of TiN and Al@sub 2@O@sub 3@ films on microfabricated atomic force microscopy (AFM) probes. These films are grown using a pulsed mode DC Magnetron sputtering technique. This method allows us to extend the range of traditional DC magnetron sputtering to a wider range of conductivities for oxide and nitride film growth. The TiN thin films tend to grow in a highly stressed manner which can cause severe deformations of the microfabricated cantilevers. The deposition of a thick interfacial Ti layer, increased growth temperature, and the use of pulsed mode deposition are effective in producing usable cantilevers. The Al@sub 2@O@sub 3@ films have been produced with both Ti and Al interfacial layers with less cantilever deformation than the TiN coating, indicating only moderate stress of the Al@sub 2@O@sub 3@ films. These studies indicate that an interfacial layer is essential for adhesion and that Al layers result in lower interfacial stress as compared to Ti layers. Resistivity, XPS and AFM measurements have been used to characterize blanket films grown by the same methods. Specialized samples are used to measure the tip shape and the conductive tips are used as point contacts to characterize the electrical properties.

SS-WeP11 Vibrationally Activated Dissociative Adsorption of CO@sub2@ on Ni(100)*, **C.L. DiCologero**, A.L. Utz,* Tufts University

We will present recent results from our study of the dissociation of vibrational-state-selected CO@sub2@ on Ni(100). Previous studies@footnote 1@ have shown that the reaction is enhanced by increasing the average thermal vibrational population of the CO@sub 2@ molecules. In our study, infrared laser excitation of CO@sub 2@ in a supersonic molecular beam produces molecules with a well-defined translational energy in a particular vibrational and rotational state. Quantifying the efficacy of energy in a specific rovibrational coordinate reveals key aspects of the potential energy surface governing the interaction. @FootnoteText@ @footnote 1@ M.P. d'Evelyn, A.V. Hamza, G.E. Gdowski, R.J. Madix, Surface Science, 167,451,(1986).

SS-WeP12 W-Si(111) Force Interaction Measurements with Force-feedback Force Sensor*, R. Erlandsson,* Linkoping University, Sweden*; **V. Yakimov**,* McGill University, Canada

We have investigated the tungsten-silicon contact in ultrahigh vacuum using an atomic force microscope equipped with a force-feedback force sensor. The operation of the sensor is based on balancing the tip-sample interfacial force by an electrostatic actuator. The measurements show that the force changes in discrete steps both upon approach and retraction, and the magnitude of the steps indicate that these events can be attributed to neck formation and relaxation phenomena involving only a few atoms. The data is in good agreement with previously published molecular dynamic simulations of the behaviour of sharp tips interacting with surfaces. It is shown that the commonly used calculation of the long-range van der Waals force using a spherical tip approximation is inadequate for measurements on this scale. Curves obtained using force-feedback method are compared with conventional force curves, and the role of the dynamic behaviour of the force-feedback sensor in the interpretation of force spectroscopy data will be discussed.

SS-WeP13 CC Bond Breaking Before CH Bond Breaking on a Metal Surface*, **S. Lavoie**, A. Adnot, P.H. McBreen, M. Castonguay,* Université Laval, Canada

CC bonds are very rarely broken before CH bonds in the same molecule, despite the fact that they are weaker. Intense research in organometallic chemistry is aimed at the selective activation of CC bonds, however examples of selective CC bond scission are usually restricted to strained ring molecules. In contrast, this RAIRS and SSIMS study shows the selective CC bond scission of methyl pyruvate on Ni(111) leading to the formation of adsorbed methoxycarbonyl and acetyl groups. The novel surface chemistry revealed in this study is also of interest due to the fact that the hydrogenation of methyl pyruvate is a test case reaction in heterogeneous chiral catalysis.

**SS-WeP14 Rovibrational State-Selected Studies of CD@sub 3@H on Ni(100)*, R.R. Smith,* *A.L. Utz,* Tufts University

Previous results in our laboratory have demonstrated the effects of rovibrational excitation in the dissociative chemisorption of methane on Ni(100). In an effort to further probe the dynamics of this system, we have recently begun state-selected experiments of the molecule CD@sub 3@H on this surface. Replacing three hydrogen atoms with deuterium removes the spherical top symmetry and changes the nuclear motions of the normal modes. This gives us access to a nearly pure C-H stretching vibration (@nu@@sub 1@) and, by using polarized laser light, allows us to investigate the effects of the incident molecular orientation. This provides us with a method to more accurately probe the transition-state and may shed light on the role that dynamical steering plays in this reaction. In a related study, we have also been investigating the collision-induced absorption and collision-induced recombinative desorption of hydrogen on this surface. Our most recent results of these topics will be presented.

**SS-WeP15 Conformation of Model Self-assembled Monolayers Studied by Sum-frequency Generation Spectroscopy*, M.B. Raschke,* *P.B. Miranda, X. Wei, Y.R. Shen,* University of California, Berkeley

Potential technological applications of self-assembled monolayers (SAM) as lithography resists, lubricants or biosensors make detailed surface strucural analysis of these materials highly desirable. In this respect chemisorbed films of model self-assembling n-alkyl monolayers have been investigated by means of infrared-visible sum-frequency generation spectroscopy providing information about chain orientation and internal molecular conformation. The trans-gauche transformation behavior of n-Octadecyltrichlorosilane (OTS) and Octadecyldimethyl(3-trimethoxysilyl-propyl)ammonium chloide (DMOAP) adsorbed on quartz with different surface molecular densities has been studied in vacuum for temperatures between 100 and 450 K. Whereas tight packing sterically prevents low energy excitations (e.g. molecular tilt, gauche defects), for low chain-densities large number of gauge conformations are found even at low temperatures. This corresponds to an observed increase in the onset temperature for chain melting with increasing surface density. For high chain densities metastable conformations (e.g. entanglement with neighboring molecules) can persist even at T=300 K and may be annealed at elevated temperatures. The observed behavior will be discussed in terms of the thermodynamics describing linear chain molecules.@FootnoteText@ Work supported by DOE.

**SS-WeP16 X-ray Photoelectron Spectroscopy Measurements of Mid-gap Density of States in Amorphous Hydrogenated SiC Thin Films*, F.S. Ohuchi,* *M.-H. Lee, D.A. KuKuruznyak,* University of Washington

Optical properties of amorphous Si-C thin films are directly related to electronic structure. The most significant optical parameters in amorphous systems are the optical band gap, E@sub g@, and the steepness parameter of the exponential absorption edge called Urbach energy, E@sub u@. In amorphous materials such as amorphous hydrogenated SiC (a-Si@sub 1-x@C@sub x@:H) thin films, the absorption edge is not clearly defined, and the Urbach tails further complicate the electronic band structure due to the mid-gap energy states. By fabricating metal-semiconductor junctions, electrons can be externally supplied to the mid-gap states. When an insulating layer further exists between the metal and a-Si@sub 1-x@C@sub x@:H thin film, occupied electrons in the mid-gap states will induce charges in the insulator, resulting in a shift in the electron binding energy at the interface, thus the density of mid-gap states can be measured by X-ray photoelectron spectroscopy (XPS). In this talk, a new method to evaluate the mid-gap density of states is proposed and applied to a-Si@sub 1-x@C@sub x@:H thin films. Experimentally, a-Si@sub 1-x@C@sub x@:H was deposited on the top of Au surface on Si by DC plasma enhanced chemical vapor deposition. Very thin oxide (SiO@sub 2@) and Au layers with the thickness of below electron penetration depth were grown subsequently. The shift in difference between Au 4f and Si 2p core-level binding energies was measured by XPS as a function of the bias voltage. The energy distribution of mid-gap DOS was obtained from analyzing the amount of the bias-induced binding-energy shift, and the measured mid-gap DOS was further compared to optical absorption measurements in an attempt to elucidate the relationship between the optical property and electronic structure in a-Si@sub 1-x@C@sub x@:H thin films.

**SS-WeP17 CO Adsorption on Au{110} and Au/TiO@sub 2@*, D.C. Meier,* *V. Bukhtiyarov, D.W. Goodman,* Texas A&M University

A great deal of interest has been generated by the catalytic properties of gold nanoclusters on metal oxide supports. These complex systems will be better understood if they are first dissected into their simplest components and studied separately. After comparing and contrasting the behavior of the components to the behavior of the system of interest, conclusions can be drawn as to the function of the catalytic system. With this information, steps can be taken to optimize those properties with the most desirable catalytic effects. IRAS studies of the dynamics of CO adsorption on the Au{110}(1x2) and Au{110} unreconstructed surface were performed as a function of CO pressure and sample temperature. The CO IRAS absorption shifted from 2118 cm@super -1@ to 2108 cm@super -1@ with increasing coverage on the reconstructed surface while the unreconstructed sample exhibited no shift, remaining at 2108 cm@super -1@. Clausius-Clapeyron data analysis yielded a E@sub a@ for CO adsorption of 12 kcal/mole at low coverages and 9 kcal/mole at elevated coverages, where the phase change appears at approximately 0.17 monolayers. These results are compared and contrasted to CO adsorption on Au/TiO@sub 2@ systems, which exhibit similar wavenumber shifts, but at higher adsorption energies.

**SS-WeP18 Adsorption, Decomposition and Stabilisation of 1,2-dibromoethane on Cu(111)*, A.S.Y. Chan,* University of Nottingham, UK*; R.G. Jones,* University of Nottingham, UK, U.K.

The molecular adsorption and thermal reaction of 1,2-dibromoethane (DBE) on Cu(111) has been studied using Ultraviolet Photoelectron Spectroscopy (UPS), work function change (@Delta@@Phi@) measurements, Low Energy Electron Diffraction (LEED) and Line-of-sight Temperature Programmed Desorption (LOSTPD). At 100 K, DBE adsorbs molecularly, exhibiting a decrease in work function of 0.86 eV at the completion of the monolayer. Layer-by-layer growth is observed up to two molecular layers, with further adsorption leading to the growth of tower crystallites. The first layer of DBE undergoes thermal decomposition at 120 K to give gaseous ethene and chemisorbed bromine in a (@sr@3x@sr@3)R30° structure, which increases the work function of the surface by 0.58 eV. Chemisorbed bromine from partial decomposition of the first layer is found to stabilise the remaining DBE molecules in the decomposing layer, thereby arresting complete decomposition until a higher temperature, leading to the emission of ethene at 140 K and 160 K for decomposition of the surface DBE layer in the submonolayer and multilayer regime respectively. The possibility of the ethene product being stabilised by co-adsorption adjacent to the chemisorbed bromine is discussed.

**SS-WeP19 Methyl Nitrite: Potential Intermediate in Methane-assisted Reduction of Nitric Oxide*, L.J. Deiner,* Harvard University*; S.W. Wilke,* California Institute of Technology*; C.M. Friend,* Harvard University

Reactions of methyl nitrite (CH@sub 3@ONO) on O-covered Mo(110) were studied in order to determine if methyl nitrite is a possible intermediate in the methane-assisted reduction of NO. The product distribution in temperature programmed reaction studies depends on the coverage of CH@sub 3@ONO. At saturation coverage, there is low temperature desorption of CH@sub 3@ONOand NO (160 K)and high temperature desorption of methyl (CH@sub 3@) radicals (650 K). At low coverage, the only products detected in temperature programmed reaction are CH@sub 3@ radicals at 650 K. Isothermal reaction experiments performed at 100 K and 300 K indicate that N@sub 2@O and NO are evolved directly into the gas phase. At both temperatures, N@sub 2@O evolution occurs first and then decreases rapidly as NO production rises. NO continues to desorb until saturation coverage of CH@sub 3@ONO. Fourier transform infrared spectroscopy confirms the results of the temperature programmed reaction and isothermal experiments. The infrared spectrum of the low coverage surface displays only one band corresponding to the C-O stretch of methoxy. The infrared spectrum of the saturation coverage surface possesses bands corresponding to intact CH@sub 3@ONO, NO, and methoxy. Upon heating the surface to 450 K, only the methoxy bands remain.

**SS-WeP20 Technique for Optical Lever Calibration for Surface Stress Measurements*, P.J. Williams,* *M. Godin, V. Tabard-Cossa, P. Grutter,* McGill University, Canada

The atomic force microscope (AFM) is increasingly being used not just to image surfaces of interest but also to probe the mechanical properties of the surface, using force spectroscopy for example. In addition, AFM cantilevers are being used as the basis of nanosensors to measure a variety of signals, including surface stress, temperature etc. In all of these applications, it is important that the relationship between the output of the position sensing detector (PSD) and the deflection of the cantilever be well known. In this poster we present a new technique for determining this relation. We attach a small resistive heater to the cantilever chip to induce a bending through the bimetallic effect. We simultaneously monitor the deflection of the beam with a fibre optic interferometer that is brought up to the backside of the cantilever and with a PSD. The interferometer fibre is positioned to be at the focus of the laser beam and hence we are measuring the deflection of the cantilever at the same position that the laser spot is focused. By computing the power spectrum of the interferometer output versus the PSD output, the PSD can be accurately calibrated. We have employed this calibration technique in a measurement of the surface stress associated with the formation of a self assembled monolayer of alkanethiol on gold.

SS-WeP21 The AFM Study of the Growth Process of a-Si:H Films Deposited by Low Frequency PECVD*, B.G. Budaguan,* ***M.N. Meytin,*** Moscow Institute of Electronic Technology, Russia*; A.A. Aivazov,* UniSil Corp.

In this work the growth process and surface morphology of a-Si:H films fabricated by the low frequency (55 kHz) PECVD at substrate temperatures from 40°C to 325°C was investigated.The results of the mass-spectra measurements of LF plasma have shown the presence of SiH3 and Si2Hx radicals.We detected large powder particles in plasma by laser beam scattering.The intensity of Si2Hx mass spectra peaks as well as the intensity of laser beam scattering decrease with the Ts increase, indicating on the decreasing of the probability of polymerization processes. The AFM analysis of a-Si:H surface reveals the island type morphology. The average diameter of islands increases with Ts, while the concentration of islands decreases. The dependence of the RMS roughness,w, on the thickness of the films,d, is w~d^b,where b~6. The high value of b (b>0.5 for a conventional 13.56MHz PECVD) and the dependence of islands diameter on Ts are proposed to be due to the participation of powder particles in the film growth. In that case the formation of a-Si:H surface morphology is controlled by two types of precursors-SiH3 radicals and powder particles. We performed computer modeling of the growth process. The initial diameter of islands formed from the powder particles and the rate of islands formation,Ci, were determined by the fitting of simulated RMS and islands diameter distribution to the experimental data. It was found that Ci decreases with increase of Ts,which correlates with the experimental data. The dependence of the island diameter on Ts is explained by the participation of SiH3 radicals in the growth process. The sticking of the SiH3 radicals to the film surface leads to the growth of island diameter, which is restricted by the boundaries of the neighbor islands. So,the higher the number of islands the lower their diameters and vice verse. This mechanism of island growth allows to explain the increase of the island diameter with the substrate temperature.

SS-WeP22 Effects of Low Dose Ion Bombardment Upon the Hg-distribution in a CeO2-layer in a TL-lamp*,* ***C. Van der Marel,*** Philips Electronics, The Netherlands*; V.H. Hildenbrand,* Philips Research, The Netherlands

Experiments have been done with a TL-lamp of which the inside was coated with CeO2. After a long time of operation the Hg vapor pressure in the lamp was too low to sustain the plasma. ARXPS was applied to determine the chemical state of the Hg and to obtain information about the depth-distribution of the Hg in the upper few nm of the CeO2-layer. Additionally experiments were done with a low flux, low energy ion beam (0.5 kV). The dose was chosen such that, even when a sputter yield of 1 is assumed, much less then 1 ML might be removed. The influence of successive ion bombardments upon the Hg-distribution was investigated. It is found that even low dose ion bombardment, in which only a small fraction of the surface is directly hit by the ions, has an important influence upon the depth distribution of the Hg within the layer.

SS-WeP23 Electron-Stimulated Desorption of Europium Atoms from Oxidized Tungsten Surfaces*,* ***V.N. Ageev,*** *Yu.A. Kuznetsov,* A. F. Ioffe Physico-Technical Institute, Russia*; T.E. Madey,* Rutgers, The State University of New Jersey

We have measured the electron-stimulated desorption (ESD) yield for neutral europium (Eu) atoms from Eu layers adsorbed on oxidized tungsten surfaces, as a function of electron energy, europium coverage, degree of oxidation of tungsten and surface temperature. The objective is to compare ESD of multivalent Eu with ESD of monovalent alkali atoms, studied previously. The measurements have been carried out using a time-of-flight method and surface ionization detector. The Eu ESD desorption yield is a complicated function of Eu coverage, electron energy E@sub e@ and substrate temperature. In the coverage range 0.05 to 0.35 monolayers (ML), thresholds for Eu desorption are observed at electron energies E@sub e@ of 25 and 37 eV, and are associated with Eu 5p and 5s excitations. Additional features (resonant-like peaks) are seen at E@sub e@ = 50 eV and 80 eV; these are associated with W 5p and 5s, respectively, and are observed even for Eu coverages > 1 ML. The Eu yields at 25 and 37 eV vanish above 330K, whereas the yields at 50 and 80 eV persist above 500K. This is the first report of ESD of metal atoms in which threshold features correlate both with adsorbate excitation energies and substrate excitation energies.

SS-WeP24 Optical and STM-based Excitation of Adsorbed Molecules: Elucidating their Elementary Mechanisms and Novel Experiments*,* ***L. Bartels,*** University of California, Riverside*; E. Knoesel, D. Moeller, T.F. Heinz,* Columbia University*; S.W. Hla, G. Meyer, K.H. Rieder,* Free University Berlin, Germany*; D. Velic, A. Hotzel, M. Wolf,* Fritz-Haber-Institute, Germany*; P. Saalfrank,* University College, England

Photodesorption and other photochemical reactions have been studied for a long time and lately using femtosecond laser pulses extremely detailed measurements could reveal an astonishing amount of their underlying elementary steps in the time domain. The scanning tunneling microscope, initially invented as a tool to image surfaces at atomic resolution, has in the meantime developed into a highly precise and powerful means to manipulate them. It could be shown that some of the excitation mechanisms relied elementarily on electron attachment to a molecular resonance. This is very similar to photoelectron attachment, but while STM has poor inherent temporal resolution, its superior spatial resolution can trace down reactions to specific adsorption sites and molecular arrangements. In this contribution a comparison of both excitation methods is given and for the induced lateral movement of CO on copper the results are compared. Further results from STM induced measurements are shown.

SS-WeP25 Atomic Resolution Imaging of Si(100)2x1-H Surface with Non-contact AFM*,* ***A. Yoshimoto****, Y. Sugawara, S. Morita,* Osaka University, Japan

Noncontact Atomic Force Microscopy (NC-AFM) have achieved true atomic resolution in 1995. NC-AFM is one of the most promising tools for surface analysis of materials including insulators on an atomic scale. In fact, many experimental groups reported atomically resolved images on various surfaces. NC-AFM imaging mechanism which contributes to the image contrast is still in progress. Although NC-AFM imaging mechanism has been investigated mainly on a chemically reactive surfaces such as semiconductor surface (Si(111)-7x7, Si(111) r3xr3-Ag etc.), there is no report on a comparative study between a reactive surface and an inactive surface using the same tip. In the present experiments, we performed the NC-AFM imaging on reactive Si(100)-2x1 reconstructed surface with dangling bond and inactive hydrogen- terminated Si(100)-2x1-H surface without the dangling bond. As a force sensor, we used a silicon tip with dangling bond, which was cleaned by Ar ion sputtering. As a result, by using the same tip, we succeeded in obtaining atomic resolution images on Si(100)-2x1 reconstructed surface and Si(100)-2x1-H monohydride surface. We found that the distance between bright spots of AFM images increased by the hydrogen termination. This suggests NC-AFM has capability for hydrogen atom imaging of Si (100) 2x1-H on an atomic scale.

SS-WeP26 Desorption Induced Change in Surface Stress of Self-assembly Alkanethiol Monolayer on Gold*,* ***A.N. Itakura,*** National Research Institute for Metals, Japan*; T. Narushima,* University of Tsukuba, Japan*; M. Kitajima,* National Research Institute for Metals, Japan*; R. Berger,* IBM SSD GmbH, Germany

Self-assembled monolayers such as alkanethiol, -HS-(CH@sub 2@)@sub n-1@-CH@sub 3@ for n=4,6,8,12, on metal surface have been well studied because they have potential use in the wide range of technological applications such as molecular recognition and nanofabrication. The alkanethiol monolayer on gold induces a compressive surface stress during the self-assembly and the saturation value of the compressive stress is directly proportional to the alkyl chain length. There are few papers on the stress induced by the desorption. Here we present the evolution of surface stress during adsorption and desorption of self-assembly alkanethiol monolayers (SAM). The adsorption of SAM (n=12) produces a compressive stress of 0.18 N/m in air. An exposure to an argon plasma, in a UHV system, induces a rapid decrease of the compressive stress. This is because of the desorption of SAM, and if the adsorption and desorption are a reversible reaction then the final stress should be zero. But actually, the final value of the stress is tensile : -0.12 N/m. After the stress experiment we examined the surface with Auger electron microscope and detected S remaining on the surface. It suggests that the removing of dodecanethiol is not as a molecule but a part of alkyl chain which is cut from adsorbed molecule. The tensile stress should be due to the remaining part.

SS-WeP27 HREELS on CO/Rh(111): Lateral Interactions in Adsorbate Layers and Vibrational Frequency Shifts*, **R. Linke,*** Eindhoven University of Technology, The Netherlands*; J.W. Niemantsverdriet,* Eindhoven University of Technology, The Netherlands, Netherlands

Lateral interactions in CO adlayers on Rh(111) were studied by HREELS and TDS. At low coverage CO adsorbs only on-top. From about 0.5 ML also the 3-fold hollow site becomes populated. The occupation of the second adsorption site is accompanied by the development of a low temperature shoulder in the TDS peaks indicating increasingly repulsive interactions in the adsorbate layer. A continuous shift to higher frequencies of the internal C-O vibration is observed over the whole coverage range. At low coverage the on-top Rh-CO frequency hardly shifts but undergoes a shift to lower frequencies upon the emergence of the 3-fold hollow. To assess the origin of the frequency shifts we measured isotopic CO mixtures. HREEL spectra of 12CO and 13CO mixtures at total CO coverage of 0.33 ML proof that the frequency shifts arise purely from dipole-dipole coupling. We also used a fixed low 13CO coverage to monitor the frequency shifts in a changing 12CO matrix. The internal 13C-O frequency remains at its singleton frequency until 0.5 ML total CO coverage, then a pronounced shift to higher frequencies begins. This testifies that at low coverage (<0.5 ML) frequency shifts arise from dipole-dipole coupling while at high coverage (0.5 - 0.75 ML) also chemical effects contribute to a large extent.

SS-WeP28 Evidence for Two Chain Length Distributions in the Polymerization of Formaldehyde on Cu(100)*, **T.R. Bryden,** S. Garrett,* Michigan State University

The adsorption of formaldehyde on Cu(100) has been studied using electron energy loss spectroscopy (EELS) and temperature programmed desorption (TPD). At 85 K, formaldehyde (H@sub 2@CO) spontaneously polymerized to form a monolayer of poly(oxymethylene) (POM). Thermal decomposition/desorption of the polymer monolayer occurred via two kinetically different routes, producing two peaks in TPD that can be attributed to molecular H@sub 2@CO generated via depolymerization of the polymer. The presence of two polymer desorption peaks has not been previously observed in studies of formaldehyde adsorption on metal surfaces. The zero and first order features observed are attributed to chain length differences present between the species and can be explained using rate equations describing the production of monomer. Our data seems to indicate the number of chains, for the zero order species, is fixed while the degree of polymerization is changing as the amount of POM formed increases. EELS spectra, taken as a function of anneal temperature, indicate the two species are similar and show losses due to POM. However, the losses due to POM for the second species are lower in intensity and new modes are identified that are attributed to the end groups of the polymer, which is consistent with shorter chains. Additionally, the second species is more ordered relative to the mixture, which could account for the enhanced production of the first species during dosing experiments where the surface is covered with the second species during exposure to H@sub 2@CO.

SS-WeP29 Photon-stimulated Ion Desorption from Mono- and Multi-layered Silicon Alkoxide on Silicon by Core-level Excitation*, Y. Baba,* Japan Atomic Energy Research Institute, Japan*; **G. Wu**, T. Sekiguchi, I. Shimoyama,* Japan Atomic Energy Research Institute

Photo-induced processes at semiconductor surface are of great importance for the fabrication of semiconductor devices, because surface modification at low-temperature is possible using photons as a driving force of the reaction. For the deposition of silicon dioxide on silicon, silicon alkoxide is widely used for the source material. Synchrotron radiation (SR) has advantages as light source of photo-induced deposition, because of the potentiality of the element-selective and site-selective reactions due to the localized nature of inner-shell electrons. Here we present the results for the fragment-ion desorption from tetramethoxylsilane (TMS) on silicon using monochromatized SR beam around the Si K-edge. In order to separate the photochemical processes induced by substrate excitation and adsorbate excitation, we have prepared well-defined monolayer, bilayer and multilayer of TMS on Si (100). In the X-ray absorption near-edge structure (XANES) spectrum taken by total electron yield, the peak energy of the resonant excitation from Si 1s to unoccupied @sigma@* orbits for TMS was shifted to higher energy by 6 eV than that for silicon substrate. For monolayer, the desorbed fragment was only CH@sub 3@@super +@ ions. Although the XANES spectrum of monolayer was almost the same as that for silicon substrate, the photon-energy dependences of the CH@sub 3@@super +@ yield followed the XANES spectrum for TMS. The results show that the secondary electrons produced by Auger decay in silicon substrate scarcely contribute to the CH@sub 3@@super +@ desorption. And it was elucidated that the core-to-valence resonant excitation in adsorbed molecule is the main cause of the molecular-ion desorption.

SS-WeP30 Formate Synthesis on Cu(111) by an Eley-Rideal Mechanism*, **M. Sano,*** University of Tsukuba, Japan*; T. Fujitani,* National Institute for Resources and Environment, Japan*; J. Nakamura,* University of Tsukuba, Japan

We have studied the kinetics and the mechanism of the formate synthesis by the hydrogenation of CO@sub 2@ over a Cu(111) model catalyst. The pressure dependence of H@sub 2@ and CO@sub 2@ upon the formation rate of the formate suggested that this reaction proceeds by an Eley-Rideal (E-R) mechanism. We thus examined the formate synthesis by the reaction of gaseous CO@sub 2@ and adsorbed hydrogen on Cu(111), where the experiments were carried out by an in-situ IRAS apparatus with a closed high pressure (1 atm) reactor. The Cu(111) sample was first exposed to 380 Torr H@sub 2@ to prepare a H/Cu(111) surface. Then, the formate synthesis was performed by exposing H/Cu(111) to CO@sub 2@ (380 Torr), where the sample temperature was constant at 308 K while the gas temperature was varied from 310 to 328 K. It was clearly shown that the bidentate formate species was formed on Cu(111) from the reaction of gaseous CO@sub 2@ and adsorbed hydrogen by IRA spectra. Moreover, the initial formation rate of the formate species increased with the heating temperature of gaseous CO@sub 2@ , indicating that the gaseous CO@sub 2@ temperature affects the formation rate of the formate synthesis. The activation energy and the pre-exponential factor of the rate constant were in good agreement with those of formate synthesis from CO@sub 2@ and H@sub 2@ at 760 Torr (P@sub CO2@ /P@sub H2@ = 1). The results mean that the formation rate of the formate synthesis only depends on CO@sub 2@ temperature, further indicating that the formate synthesis proceeds by the direct reaction between gaseous CO@sub 2@ and adsorbed hydrogen. We thus concluded that formate synthesis proceeds by an E-R mechanism.

SS-WeP31 Surface Treatment and Characterization of PMMA, PHEMA, and PHPMA*, **H. Lim,*** Korea University*; Y. Lee,* Korea Institute of Science and Technology*; J. Cho,* Hanyang University, Korea*; S. Han,* Korea Institute of Science and Technology*; K.-J. Kim,* Korea University

Poly(methyl methacrylate)(PMMA), poly(2-hydroxyethyl methacrylate)(PHEMA), and poly(2-hydroxypropyl methacylate)(PHPMA) were modified to improve the wettability using two methods: plasma treatment and Plasma Source Ion Implantation(PSII) treatment. The modified surfaces were characterized to investigate the dependence of polymer structure on the treatment conditions and hydrophobic recovery behaviors. The contact angle measurement was used to calculate the surface free energy. The polar component of surface energy is a dominant factor to improve the wettability. The changes of surface functionality were observed with XPS and ATR-IR. PSII treatment has provided much more various functional groups on the surface and deeper modified layer than plasma treatment during the same treatment time. The surface morphology was investigated by SEM and AFM after treatment. However, the severe surface alteration was not observed. The difference of experimental conditions among the polymers was interpreted by the glass transition temperature which is related to the structure of each polymer.

SS-WeP32 Coadsorption of CO and O@sub 2@ on W(110) Surface*, K.-H. Lee, H.-S. Han, H.-G. Yun, **T.S. Yang**, J.-H. Boo, S.-B. Lee,* Sungkyunkwan University, Korea*; H.T. Kwak,* Kookmin University, Korea

The coadsorption of CO and O@sub 2@ on W(110) surface was studied by LEED, TDS, and photoelectron spectroscopy. In the TDS for the coadsorption of CO at RT on O@sub 2@ precovered W(110) surface, two CO desorption states were observed at about 400 and 1150 K, called @alpha@ and @beta@, respectively. The @beta@-CO spectra with second order desorption kinetics were shifted to lower desorption temperature as increasing the amount of preadsorbed atomic oxygen on the W(110). Moreover, the @beta@-CO spectra were gradually increased with increasing the amount of preadsorbed oxygen to 0.5 ML. Even though a (2x1) LEED pattern appeared during oxygen adsorption at RT and 1-3 L oxygen exposures, we didn't observe any new pattern induced by CO in this study. Only the structure of c(11x5) was obtained at temperature in their range of 800-1100 K. These results indicated that there were interaction between CO and O and thereby the @beta@-CO might not be dissociated even at the higher temperature than 800 K. By using the XPS and UPS, it was also confirmed that the coadsorbed @beta@-CO at 950 K doesn't dissociate as the experimental results of the adsorption of pure CO on W(110) surface at the same temperature. According to the valence band spectra, two CO peaks at near 10.7 eV(4@sigma@) and 7.0 eV(5@sigma@+1@pi@) were observed, indicating molecular CO adsorption on the oxygen preadsorbed surface at RT. Even heating the coadsorbed surface to 950 K, we could also detect the CO 4@sigma@ peak that can be an important factor for identifying a contribution of the CO 4@sigma@ molecular orbital to the CO-metal bond. To our best knowledge, this is the first report and quite contradictory result to that reported previously.

SS-WeP33 Effect of the Sample Topography on the Adhesive Force in Atomic Force Spectroscopy Measurements in Air*, **N. Nakagiri,*** Nikon Corporation, Japan*; L. Sirghi,* Nagoya University, Japan*; K. Sugisaki,* Nikon Corporation, Japan*; H. Sugimura, O. Takai,* Nagoya University, Japan

It is widely recognized that water thin films formed on probe and sample surfaces greatly affect the atomic force microscopy (AFM) measurements in air. Generally, the interaction between the probe tip and sample surface is a result of superposition of van der Waals, electrostatic, capillary and interfacial tension forces. The latter two forces arise due to water thread usually formed at tip-sample contact region in air and their contribution to the tip-to-sample adhesive force is dominant The effect of local curvature of sample surface on the capillary and interface tension adhesion force of water meniscus formed between AFM tip and sample in air is demonstrated both, theoretically and experimentally. An analytic solution for capillary and tension adhesive force is founded under approximation of thermodynamic equilibrium of a symmetric water meniscus formed at the tip-sample contact region. It is shown that the sample local curvature strongly affects the water meniscus geometry and the adhesion force. Compared to the force computed for a null local curvature of the sample surface, the theoretical model predicts larger/smaller adhesive force for concave/convex local curvature. The theoretical predictions were confirmed by experiment. Atomic force spectroscopy measurements were performed for a silicon nitride cantilever and a standard sample of quartz patterned with 3x3 mm2 in area and 20 nm in depth grooves and platinum covered. Maps of sample surface topography and adhesive force have shown a much small/large force on the high/low part of groove edges, where the sample local curvature is convex/concave.

SS-WeP34 Surface Electronic Structure of Rare Gas Xe on Cu(111): A Scanning Tunneling Microscope Study*, **J.-Y. Park,** U.D. Ham,* Seoul National University, Korea*; S.-J. Kahng,* University of Illinois at Urbana-Champaign*; Y. Kuk,* Seoul National University, Korea

A newly built ultrahigh vacuum cryogenic scanning tunneling microscope (STM) was used to study the modified surface state and image state on an adsorbate-covered surface, one monolayer (ML) Xe on Cu(111). Electron standing waves were observed on 1 ML Xe-covered Cu(111) as well as on bare Cu surface. By carefully controlling the Xe coverage, standing waves on both bare Cu surface and 1 ML Xe-covered Cu surface could be observed simultaneously in one STM image. Therefore, any possibility of artifact due to different conditions of the tunneling tip can be ruled out. The wavelength of standing waves on Xe layer is ~15% longer (~17Å) than that on Cu surface at sample bias as low as 10meV. By performing scanning tunneling spectroscopy on this surface, dispersions of the surface state both on Xe layer and bare Cu surface are determined. It was found that the onset of the surface state is shifted towards Fermi level by (130±20) meV and the effective electron mass is slightly larger on Xe layer than on bare Cu surface. The electronic lifetime, the multilayer effect, and the effect of image states will also be discussed.

SS-WeP35 STM Barrier-Height Imaging of Alkali Adsorbed Si(111)7x7*, **S. Kurokawa,** A. Sakai,* Kyoto University, Japan

The chemisorption of alkali metals on silicon is one of the most studied adsorption systems, and a large number of theoretical and experimental investigations have been carried out to understand its atomic and electronic structures. However, little has been known on atomic-scale properties of the K adsorption on Si(111)7x7. Hashizume and his coworkers have investigated the initial stage of K adsorption on Si(111)7x7 by STM, and identified some adsorption geometries of K. They also concluded that the bonding between K atoms and Si(111)7x7 surface atoms changes from ionic when K atoms adsorb individually to weakly covalent when they form clusters. We have performed STM imaging and local barrier-height (BH) measurements upon adsorbed K atoms and clusters. The K coverage is about 0.01ML, which corresponds to a very initial stage of adsorption. We found that the local BH decreases at K cluster and each single K atom. The average BH reduction at the K adsorbed site is -1.9 eV under positive sample bias where the electronic structure of tip has little influence on the BH. According to recent photoemission experiments, the reduction of the work function at the saturation coverage of K is -2.9 eV. The measured BH reduction at K sites is smaller than this value but can be a plausible value since the K-Si bonding at the initial stage of adsorption may be different from that in a K overlayer at the saturation coverage. @FootnoteText@ @footnote 1@ T. Hashizume, K. Motai, Y. Hasegawa, I. Sumita, H. Tanaka, S. Amano, S. Hyodo and T. Sakurai, J. Vac. Sci. Technol. B9, 745 (1991).

SS-WeP36 Laser Etching of Si with NF3 using CuBr Laser*, **B. Ivanov,** K. Woynov,* University of Chemical Technology & Metallurgy, Bulgaria*; M.P. Tarassov,* Central Laboratory of Mineralogy and Crystallography, Bulgaria*; L. Zambov, V. Shanov,* University of Chemical Technology & Metallurgy, Bulgaria

Laser induced thermal etching of Si using focused copper bromide vapor laser beam with wavelengths of 510 and 578 nm on monocrystalline Si (100) with NF3 gaseous phase was presented. The laser average power was in the range 4-10 W with repetition rate - 20 kHz and pulse duration - 60 ns. The process parameters were varied in the ranges: scanning speed from 10 to 1000 microns/s, substrate temperature from 100 to 400 C and partial pressure in the range of 100 - 1000 mbar. The etching products were estimated on the base of thermodinamcal calculation. The width, depth and cross section of the etched channels were investigated by Scanning Electron Microscopy (SEM). Some residues on the side wall are removed by subsequent thermal wet etching in KOH solution. In some cases we find evidence for waveguiding effect of laser radiation during the laser etching. The etching rate increases with the scanning speed and is in the range of 2.10^5 - 5.10^6 micron^3/s for the scanning speed of 10 micron/s to 1 mm/s. The aspect ratio of laser etched groves are in the range of 5 - 40 for all structures and reaches 100 for waveguiding part of the trench. This very high etching rate allows using of such process for micromachining of Si. Application of this approach for production of square rods array and field emission like tips was presented.

SS-WeP37 Reactivity of CO over Au Surfaces at Elevated Pressure*, **K.F. Peters,** P. Steadman, O. Robach, J. Alvarez, S. Ferrer,* European Synchrotron Radiation Facility, France

The "Pressure Gap" in surface science separates the well-studied UHV regime from the near-atmospheric pressure regime, where gas-phase catalysis is typically employed. We present first results from a new UHV/HiP surface x-ray diffraction chamber that is capable of spanning the pressure gap over 13 orders of magnitude up to 5 bars or higher.@footnote 1@ The UHV/HiP chamber is employed here to study gas-surface reactivity of carbon monoxide over metals. The Au(111) and Pt(111) surfaces are investigated because of their known inertness to carbon monoxide in vacuum studies. Moreover, CO/Pt(111) is an archetypal model of catalysis, whereas gold is among the most inert metals and is only known to adsorb CO at cryogenic temperatures. The observed gas-surface reactions are unexpectedly strong, owing to the elevated pressures. Both CO/Au(111) and CO/Pt(111) become reactive at near-atmospheric pressures and elevated temperatures. On Au(111), the Herringbone reconstruction can be lifted under certain conditions.@footnote 2,3@ The Pt(111) surface reacts with CO to form a new structure that has never previously been observed in vacuum studies. An important feature of these two examples is that the metal atoms are displaced significantly from their natural positions, which is uncommon in traditional examples of gas adsorption. @FootnoteText@ @footnote 1@P.Bernard, K.F.Peters, J.Alvarez, S.Ferrer, Rev.Sci.Instr., 70, 2, 1999, 1478-1480. @footnote 2@Steadman et al, accepted to Phys.Rev.B @Footnote 3@Peters et al, submitted.

Vacuum Technology
Room Exhibit Hall C & D - Session VT-WeP
Poster Session

VT-WeP1 Study of Uncertainty of a Constant Volume Flowmeter*, **D. Tian,*** Lanzhou Institute of Physics, P.R. China, P.R.China*; X. Wen,* Lanzhou Institute of Physics, P.R. China

A constant volume flowmeter was built in Lanzhou Institute of Physics (LIP). It can calibrate mass flow meters. In order to find and reduce the systematic errors, its uncertainty is calculated and analyzed at first. The range of the flowmeter is 1.7x10@super-3@-85 Pam@super3@/s (1 sccm-

50 slm) with uncertainty (1@sigma@) less than 1.2%. Then, a lot of experiments are accomplished by calibrating the mass flow meters. The measurement data of two mass flow meters prove that the flowmeter has good repeatability and long-term stability. Because the systematic errors are still under discussion, we have to prove our supposition by comparison study at last. The range of constant pressure flowmeter developed in our laboratory formerly is 1x10@super-3@-10@super-8@ Pam@super3@/s, with uncertainty less than 2%. For carrying out the comparison between these two flowmeters, an accurate mass flow meter whose range is 1-10 sccm is used as transfer standard. The mass flowmeter is calibrated by two flowmeters respectively. The result shows that the agreement of these two standards is better than 1.5%. The comparison is mainly dependent on the linearity and stability of spinning rotor gauge, and the uncertainty resulting from these two factors is about 0.5%. The short-term repeatability of the mass flow meter is also an error source of comparison, and the uncertainty resulting from this factor is approximately 0.2%. The big systemic error is not found in the tests and calibration reliability has been ensured through the above discussions.

VT-WeP2 Development of the Quadrupole Mass Spectrometer with the Bessel-Box Type Energy Analyzer : Function of the Energy Analyzer in the Partial Pressure Measurements*, **N. Takahashi**, H. Akimichi, T. Hayashi,* ULVAC Japan, Ltd., Japan*; Y. Tuzi,* ULVAC Corporation, Japan

We have obtained several advantages of the newly developed quadrupole mass spectrometer (QMS) with the Bessel-Box type energy analyzer for the accurate measurement of partial pressures in high to extreme high vacuum. The analyzer is placed between the ionizer and the quadrupole assembly of QMS. The gas phase ions and the electron stimulated desorption (ESD) ions generated in the ionizer are separated by the analyzer, because of the difference of kinetic energies between them. As the overlapping of the gas phase ions and ESD ions gives the complex mass spectra, the elimination of ESD ions by the energy analyzer improves the spectra to simpler ones. The accurate measurement of partial pressures was made use of the simple mass spectra of gas phase ions which were given by the new QMS. The sensitivity of new QMS for the very small amount of impurities in the atmosphere of relatively higher pressure was also improved down to 10ppb of the total pressure owing to the reduction of background signal. The background signal is much reduced by the geometrical structure of the energy analyzer which prevents the ion collector with secondary electron multiplier from the irradiations of vacuum ultraviolet rays and soft x-rays generated in the ionizer. The discrimination between the non-dissociative molecular ions and the fragment ions with same mass to charge ratio (m/z) is also the important factor for the accurate measurement of partial pressures. The energy spectra of those ions are determined by the mechanism of ion formation such as ionization process, fragmentation process, etc. Thus, the spectra of each m/z ions are expected to apply for the discrimination mentioned above.

VT-WeP3 A Summary of Quick Disconnect Vacuum Flanges*, **M. Mapes**,* Brookhaven National Laboratory, usa

In accelerator environments especially proton machines, high background radiation necessitates the need for quick disconnect vacuum flanges. The use of quick disconnect flanges significantly reduces the dose of radiation received by workers when installing or removing vacuum chambers in the accelerator. Over the course of many years there have been many different designs used for these flanges at Brookhaven National Laboratory for such machines as the AGS, Booster and RHIC. Several different flanges with apertures as large as 14" diameter were also evaluated for use in the SNS project. A summary of various quick disconnect flanges used at Brookhaven as well as some commercially available flanges and their evaluation results are presented.

VT-WeP4 Continuous Determination of the Gas Composition during Pump-down of Vacuum Chambers*, **N. Mueller**,* Balzers Instruments, Liechtenstein, Principality of Liechtenstein*; P. Schoch,* Balzers Instruments, Liechtenstein

The gas composition during pump-down of vacuum chambers starting at atmospheric pressure is an important information for the evaluation and design of pumping stations. Nevertheless, this composition is rarely determined on-line, as there are no sensors available that directly allow for gas specific analysis over a wide pressure range. To overcome this problem, a differentially pumped quadrupole mass spectrometer with a unique inlet system has been developed. This instrument allows for continuous gas analysis in the pressure range from 1000 mbar down to 1E-3 mbar. Pump-down curves of different pumping stations (e.g. turbo-pumped systems with rotary vane pumps, diaphragm pumps etc.) have been determined. The results of these analysis will be presented and discussed.

VT-WeP5 Hydrogen Outgassing from Titanium Modified Layers with Various Surface Treatments*, **Y. Mizuno**,* Nippon Valqua Industries, Ltd, Japan*; A. Tanaka,* ULVAC-PHI, Inc., Japan*; K. Takahiro,* Tohoku University, Japan*; T. Takano, Y. Yamauchi, T. Okada, S. Yamaguchi, T. Homma,* Chiba Institute of Technology, Japan

In an extreme high vacuum (XHV) system, hydrogen outgassing is the most important factor to obtain vacuum pressure below 1.0x10@super -10@Pa. Titanium is an interesting material for applications in XHV construction. This work aims to be clear about a correlation between hydrogen outgassing and surface structures of pure titanium in vacuum technology. The titanium surfaces were prepared following treatments such as chemical (CP), electrical (EP), buffing (BP) and mechano-chemical polishing (MCP). Characterization of oxide layers has been carried out using Auger electron spectroscopy and angle-resolved x-ray photoelectron spectroscopy, and a cross section of modified layer has been observed with transmission electron microscopy and an optical microscope for metal/scale. The hydrogen distribution in a surface region was measured by using elastic recoil detection analysis. The oxide thicknesses were from 20 to 50 nm, although the finished titanium surfaces were covered with TiO@sub 2@ for CP, EP, BP and MCP, and also TiO was formed under the top layer for MCP. The thick modified layers (about 1µm) on surfaces were made in BP and MCP processing, and the modified layers had extremely high-density distribution of hydrogen (H/Ti about 1-2). Thermal desorption spectroscopy measurements indicated that the desorption behavior of hydrogen was not strongly depending on the thickness of oxide layer, and the hydrogen outgassing rates were less than 4.0x10@super -7@Pa.m.s@super -1@ at room temperature. We will report the results of the relation between the quantities of desorbed hydrogen gas and the structure of modified layers on titanium polished surfaces.

VT-WeP6 Friction Force Measurement of Type 304 Stainless Steel in a High Vacuum*, **A. Kasahara**, M. Goto, M. Tosa, K. Yoshihara,* National Research Institute for Metals, Japan

Vacuum friction measurement system based on Bowden-Leben type system was successfully developed. The system can evaluate sliding friction coefficient under changing load from 0.2N to 0.98mN and at changing atmospheric pressure from 1E+5Pa to 1E-8 Pa. The friction measurement was carried out on typical vacuum materials samples as type 304 austenitic stainless steel sheets after such surface treatments as chemical polishing, mechanical polishing or electrochemical buffing. Chemically polished steel shows the lowest friction coefficient as the decrease of the vacuum pressure and as the decrese of the load due to low desorption of adsobate on the surface. The friction measurement especially under the load less than about 10mN in an atomosheric pressure shows that surface adosobate changed by surface roughness of polished steels could have an large effect on friction force. While, the measurement under the pressure less than 1E-5Pa shows little effect by surface absobate on friction force. The measurement results therefore conclude that Amonton-Coulomb's law is valid in measuring friction force under low load in a high vacuum.

VT-WeP7 Surface Cleanness of Substrates Transported with Levitation Transfer System Installed in an Extreme High Vacuum Integrated System*, **M. Tosa**, A. Kasahara, M. Goto, K. Yoshihara,* National Research Institute for Metals, Japan*; Y.S.K. Kim, K.S.L. Lee,* Sungkyunkwan University, Korea

The extreme high vacuum (XHV) integrated process with magnetic levitation transports has been developed in order to transfer substrates among vacuum chambers without any contamination on the ultraclean surface. The XHV integrated process has five main lin e chambers, six sidetrack line chambers, connector chambers and six vacuum instrument chambers for surface analyses and film preparation. Levitation transports using superconducting magnet system and electromagnet system are installed into the line chamb ers because they have no sliding part to generate dust particles as well as outgassing which may damage the ultraclean substrate surfaces and environment. The levitation transports can transfer substrates among connected six chambers in the pressure change of less than 10@super -10@ Pa. Cleanness of transported substrates surfaces was observed by a scanning auger electron microprobe with submicron analysis area. Substrates surfaces of a copper sheet and a stainless steel sheet that were argon ion sputter-cleaned in the auger analysis chamber were kept clean without any adsorption of oxygen nor carbonate during the levitation transportation among the auger analysis chamber and the film preparation chamber. Surfaces of copper film and stainless steel film on steel substrates prepared in the film preparation chamber were also kept clean after the transportation from the film preparation chamber to the auger analysis chamber.

**VT-WeP8 Production, Installation and Performance Evaluation of Extruded Aluminium NEG-coated Vacuum Chambers for the European Synchrotron Radiation Facility (ESRF)*, P. Chiggiato*, *A. Escudeiro Santana, V. Ruzinov,* CERN, Switzerland*; R. Kersevan,* ESRF, France

In order to comply with new European rules concerning the maximum allowable radiation dose for non-exposed workers, the ESRF has started a program for reducing the pressure in the undulator straight sections. This has led to the development of new narrow-gap extruded aluminium vacuum chambers coated with a Ti-Zr-V non-evaporable getter film on the whole inner wall surface. Several aluminium chambers of different dimensions have been coated and their vacuum characteristics have been evaluated. Two of them (5 m long, 74x11 mm elliptical section), have been installed onto the 6 GeV storage ring of the ESRF. Their performances during the vacuum conditioning under an intense synchrotron radiation flux of about 10@super 17@ photons sec@super -1@ m@super -1@ will be reported, together with other details of their operation.

**VT-WeP9 Cleaning of Artificial Contamination on Aluminum Surface for Ultra-high Vacuum Treated in Supercritical Fluid and Evaluated with FT-IR*, T. Momose*, *H. Mishina,* Miyagi National College of Technology, Japan*; Y. Ikushima,* National Industrial Research Institute of Tohoku, Japan*; K. Tatenuma,* Kaken Corp., Japan*; T. Goto, M. Takahara,* Miyagi National College of Technology, Japan

To decrease outgassing rate of the surface for ultra-high vacuum materials, clean surface is required. We have paid attention on native contamination of the surface.@footnote 1@ Here, cleaning test of the artificial contamination which can be deposited on the surface during treatments is carried out using supercritical fluid(SCF) CO@sub2@ with high solubility for organic materials. Triglyceryde is selected as a contamination because it is the main ingredient of grease of human body. The triglyceryde was deposited on mirror surface of aluminum circular discs(5 mm in diameter) by evaporating ether-triglyseride solutions. The disc was kept in SCF CO@sub2@ for a half hour at 40°C and a fixed pressure. The surface was evaluated from the CH@sub2@- and CH@sub3@- peaks of FTIR spectra. The standard lines of the peaks were obtained from the ones of FT-IR as a function of the density of ether-triglyceride solution. Removing rate was calculated from the ratio, (Lo-Li)/Lo x 100 %, where Lo is the peak height before treatment and Li the one after treatment. The deposited thickness between one µm and 21 µm was proportional to a square root of density of the solution (1%-30%). Precision of removing rate was ±13 %. The removing rate was proportional to pressure, 40 to 100 % in the range from 100 atm to 250 atm, where it was 100 % in the range from 250 atm to 300 atm. The data showed that the cleaning using SCF CO@sub2@ is promising to remove artificial contamination like the ones on the order of µm thick. @footnote 1@ T.Momose et.al, JVST, A17(4), Jul/Aug, 1999, 1391.

**VT-WeP10 CESR Phase-III Interaction Region Vacuum Chamber*, Y. He*, *Y. Li, N.B. Mistry, S. Greenwald,* Cornell University

Two 115" long copper UHV chambers for the Cornell Electron Storage Ring (CESR) Interaction Region were fabricated. These chambers are a part of the "Phase-III" upgrade project for the CESR storage ring. They incorporate several novel features including a remotely engaging differentially pumped Viton O-ring sealed UHV flange, two RF shielded bellows joints, and inner stepped masking for synchrotron radiation. The fabrication of these chambers incorporates multi-stage electron beam welding to maintain the strict tolerance required for installation through superconducting and permanent quadrupole magnets. Before final welding, a series of EB welding setup tests were done to work out a welding procedure for optimizing welding parameters and avoiding contamination in the weld zone. This paper will describe the design, fabrication, welding, leak checking, and final UHV performance testing of these chambers.

**VT-WeP12 Monte Carlo Direct Simulation of Rarefied Flow in the Cylindrical Chamber of an Orifice-flow System*, Y.W. Chang*, Precision Instrument Development Center, R. O. C., Taiwan, R. O. C.

The orifice-flow system has been commonly used in the calibration and measurement of the vacuum systems. Such a system usually consists of a vacuum chamber in which two cylindrical or spherical halves separated by a plate with the orifice in the center. For the application of the orifice-flow system, calculating the correct conductance of the orifice is the most important thing to do. However the actual flow condition inside the chamber, such as the gas density distribution and gas flux distribution, also restricts the accuracy of the calibration or measurement. In this paper the flow field inside a cylindrical vacuum chamber of an orifice-flow system is investigated using the direct simulation Monte Carlo (DSMC) method. A known gas flow is introduced to the upper chamber through a port in the center of the top plate. We simulate cases in which the outlet boundary is set to be in vacuum or given a known pressure that represents a vacuum pump. The observation is focused on the pressure distribution in these cases. In each case, baffles are added in the upper and lower chamber after the flow reaches a steady state. Baffles in the orifice calibration system are used to improve the uniformity of the gas density distribution and the gas flux distribution. Therefore the variations of the pressure distribution and the velocity field in the chamber after baffles are added are particularly investigated.

**VT-WeP13 The Topology of Molecular Flow in Axial Compressor*, P.A. Skovorodko,* Institute of Thermophysics, Russia

An approximate representation of the real geometry of the axial flow compressor by its plane version is widely used in theoretical models of the gas flow in the molecular pump. To analyze the accuracy of such kind of approaches the numerical algorithm for simulation the free molecular flow in the real geometry of the compressor is developed. The algorithm is based on the well known test particle Monte Carlo method. The pumping process in the considered case is completely characterized by two values of direct and back transmission probabilities. The main problem to be solved during the simulation of molecule motion in the tract is to find the point of intersection of their trajectory, which represents a straight line, with stationary or moving surfaces of the compressor units, where the diffuse-specular reflection of molecule with some accommodation coefficient is assumed. Two types of molecular pump are considered: the Holweck pump with spiral grooves placed on the rotor, and the multi-stage turbomolecular compressor with flat-plate blades. The results obtained for real geometry demonstrate higher compression ratio and are in better agreement with available experimental data in comparison with those obtained for plane version of geometry. The difference between two approaches is higher for higher rotor speed. The main reasons for such difference are the topology of axial flow and non-inertial character of rotating system of reference. The developed algorithm may be used to optimize the design of compressor operating in the free molecular conditions.

**VT-WeP14 Rapid Cool Dual Slot Load Locks For LCD*, A. Hosokawa*, *W. Blonigan, S. Kurita,* Applied Materials Inc.

Rapid cooling of 680mm x 880mm glass substrate was demonstrated in the dual slot load locks @footnote 1@ of Applied Materials AKT 5500 CVD system. It takes 33 sec to cool the substrate from 400°C to 60°C with the uniformity of ±5°C. To accomplish this, two techniques were used. Helium equivalent to partial pressure of 9 torr was injected at the initial stage of venting. Two cooling plates were located above and below the substrate and the distance of the cooling plates was reduced to 8 mm when cooling. Rapid cool dual slot load locks reduced the system cost by eliminating expensive machined components and a more powerful pump. Uniform cooling enabled reliable substrate handling and eliminated undesirable stress on the substrate upon cooling compared with the conventional 12 slot load locks. @FootnoteText@ @footnote 1@ Shinichi Kurita, Wendell Blonigan, Akihiro Hosokawa, US Patent pending #7828.7017, Dec 1999.

**VT-WeP15 Experimental and Theoretical Study of a Differentially Pumped Absorption Gas Cell used as a Low Energy-pass Filter in the VUV Photon Energy Range*, B. Mercier*, *L. Nahon, O. Dutuit, C. Prevost, R. Thissen, G. Bellec, M. Compin,* LURE, France

In order to separate the fundamental synchrotron radiation from the high harmonics emitted by an undulator, a low photon energy-pass filter has been designed and built, insuring a high spectral purity on the VUV SU5 beamline at Super-ACO. It consists in an absorption cell filled with rare gases and separated from the ultra-high vacuum of the storage ring and of the beamline by a double differential pumping obtained with thin capillaries, and whose designed has been optimized by numerical computation of pumping speed. Admission pressures in the range of 100 Pa in the central part of the filter have used without any degradation of the upstream or downstream ultra-high vacuum. The measured attenuation factors above the energy cut-off are above 10@super 5@ and 10@super 2@ (and certainly above 10@super 3@ with ultimate pressure of Ne) for respectively argon and neon used as absorbing gas, with no measurable attenuation of fundamental radiation. A sophisticated numerical approach performed in the intermediate regime, taking into account the geometry of the whole absorption cell including the first pair of capillaries, has been developed, allowing reliable predictions of the expected attenuation coefficients for any given configuration of the filter.

VT-WeP16 DSMC Study of Plume Flows in Cryogenic Vacuum Facility*, M.S. Ivanov, G.N. Markelov,* Institute of Theoretical and Applied Mechanics, Russia

The study of plume flows has been an interesting research subject area of rarefied gas dynamics in the past. Experimental techniques and various engineering approaches were mainly employed for such studies. The recent resurgence of interest in the subject is prompted by the design of a new generation of satellites and space stations for which an accurate prediction not only of force and heat loads produced by the plumes, but also of contamination is needed. Therefore, a comprehensive study of plume structure including core flow, periphery flow and backflow is very important. For correct simulation of small thruster plumes in experimental facilities, it is necessary to have reasonable low background pressure levels. Main feature of new high vacuum plume test facilities STG (DLR) and CHAFF-IV (USC) is a novel cryogenic array, where the expanding plume gas hits a complex-structured cryosurface and freezes immediately. Nevertheless, disturbance of the plume is possible due to the penetration of condensate vapor and of plume molecules that do not stick immediately to the condensate. Therefore, it is necessary to supplement experimental modeling of plume flows by numerical simulation of the plume flow inside the facility taking into account the influence of incomplete condensation of plume molecules. It will allow one to determine a region where a plume flow is undisturbed as in space for different thruster and facility operating conditions. The main objective of the paper is a numerical study of thruster plume flows under low-density conditions in a cryogenic vacuum facility with consideration of background pressure caused by incomplete condensation of plume molecules on the cryogenic array.

Wednesday Afternoon, October 4, 2000

Biomaterial Interfaces
Room 202 - Session BI-WeA
Non-fouling Surfaces

Moderator: M. Grunze, University of Heidelberg

2:00pm **BI-WeA1 Fundamental Studies of Self-Assembling Monolayers as Model Systems for Biological Interfaces*, G. Hähner,*** ETH Zurich Switzerland, Switzerland **INVITED**

The first level of concern of interactions between proteins and synthetic surfaces deals with non-specific adsorption: that is, adsorption reflecting hydrophobic or electrostatic interaction. Chemically modified Scanning Force Microscope (SFM) probes allow it to study such interactions with surfaces separately and hence to mimic the different contributing forces to protein-surface interaction independently. Poly(ethylene glycol) (PEG) has been recognized for a long time for its outstanding protein resistant properties. The force between oligo(ethylene glycol) terminated (self-assembled) monolayers and proteins, however, depends on the conformation of the adsorbed molecules and parameters of the environment. We have studied the interaction between differently functionalized (charged and hydrophobic) SFM probes and oligo(ethylene glycol) terminated surfaces depending on the length of the ethylene glycol part, the cation in the electrolyte solution and the ion concentration of the aqueous environment.

2:40pm **BI-WeA3 Protein Adsorption and Cellular Responses to Polysaccharide Coatings*, S.L. McArthur,*** CSIRO Molecular Science and CRCERT, Australia*; P.G. Hartley,* CSIRO Molecular Science, Australia*; K.M. McLean, G. Johnson, M.L. Jenkins, H.J. Griesser,* CSIRO Molecular Science and CRCERT, Australia

There is increasing evidence that the cellular response to a biomedical implant is determined by the presence of specific proteins at the interface. There are a number of protein/surface interactions that influence such adsorption events. In this study we assess the roles of steric and electrostatic interactions on the protein adsorption characteristics of a range of cell supporting and cell-resistant polysaccharide surfaces. Polysaccharides were grafted onto highly anionic, flat, radio frequency glow discharge (rfgd) coatings with or without secondary graft supporting interlayers. Polysaccharides of differing functionality and charge density (aminodextran, carboxymethyldextran and oxidised dextran) were used. The properties of the resulting surfaces were assessed using XPS, streaming potential and AFM imaging and colloid probe force measurements. The impact of surface properties on protein adsorption was also monitored using XPS, ELISA and Surface-MALDI-MS techniques. The results of these studies indicate that protein adsorption occurs regardless of steric interactions provided an electrostatic attraction exists between the protein and the surface. To illustrate this point, surfaces were engineered which were expected to display a low affinity for cell adhesive proteins. In vitro cell studies on such surfaces showed minimal cell attachment and growth which was in marked contrast to the same polysaccharide surfaces with the proteins covalently attached. In this instance, cell attachment and growth was observed. These studies demonstrate the role of specific protein adsorption in the mediation of cellular responses on polysaccharide surfaces.

3:00pm **BI-WeA4 Film Formation of Self-assembled Monolayers of Thiol-modified Polyethylene Glycol on Gold*, S. Tokumitsu,*** *S. Herrwerth, W. Eck, M. Himmelhaus, M. Grunze,* Universität Heidelberg, Germany

The adsorption kinetics of self-assembled monolayer (SAM) of thiol-modified polyethylene glycol (PEG: 2000 dalton) on polycrystalline gold surface in dilute solution has been studied by using ellipsometry, infrared reflection absorption spectroscopy (IRRAS), X-ray photoemission spectroscopy (XPS) and second harmonic generation (SHG). Thickness and structure of the finally obtained layer exhibit strong dependence on the solvent. In-situ SHG monitoring of the headgroup adsorption of PEG from 50 µM DMF solution shows rapid coverage increase up to 44% within the first 10 min of immersion, followed by a slowly proceeding adsorption step. Final coverage is reached after a total immersion time of about 2 hours. On the other hand, ellipsometry reveals that film thickness drastically increases after 1-2 hours of immersion. These results indicate a restructuring of the PEG moiety from an amorphous to a crystalline-like phase at that time. The results for film thickness and structure obtained by in-situ and ex-situ experiments will be discussed in detail and finally a phenomenological model of the adsorption process will be presented.

3:20pm **BI-WeA5 Synthesis and Characterization of Functionalized Polymerizable Diacetylene Containing Thiol Monolayers*, N.R. Holcomb,*** Agilent Technologies*; D.G. Castner,* University of Washington*; D.W. Grainger,* Colorado State University

Self-assembled structures have been used to tailor the surface character of materials: enhance adhesion, lubrication, catalysis, and molecular/cell immobilization and recognition in biotechnology.@footnote 1,2@ Utilization of polymeric materials in the self-assembling monolayer can increase the thermal and mechanical strength of the films formed from monomeric materials.@footnote 3@ The use of polymeric blocks within self-assembled films has shown that there is added stability toward solvent attack.@footnote 4,5@ We report the synthesis and characterization of new surface functional diacetylene thiols of the formula: R-(CH2)n-C?C-C?C-(CH2)m-SH where n=m=9, and R=fluoro alkyl, or oligoethylene glycol. These materials were synthesized via multistep schemes featuring an asymmetric Cadiot-Chodkiewicz coupling to create the functional diacetylenes from pairs of alkynes. Self-assembled monolayers of these organic molecules are characterized with polarized FTIR, ellipsometry, contact angle, XPS and TOF-SIMS. Films were formed from diacetylene thiols containing contrasting surface functional groups to provide a triethylene glycol non-biofouling surface@footnote 6@ and a low surface energy fluorinated surface.@footnote 3@ @FootnoteText@ @footnote 1@ K. M. McClary, D. W. Grainger, Biomaterials, 20, 1999, 2435-2446 @footnote 2@ K. M. McClary, D. W. Grainger J. Biomed. Mater. Res., in press (2000). @footnote 3@ Ebert, R.; Laschewsky, A.; Ringsdorf, H.; J. Am. Chem. Soc. 1985, 107, 4134 @footnote 4@ Sun, F.; Grainger, D.W.; J. Polym Sci. Polym. Chem. Ed. 1993, 31, 172 @footnote 5@ Sun, F.; Castner, D.G.;Grainger, D.W.; Langmuir. 1993, 9, 3200 @footnote 6@ Pertsin, A. J.; Grunze, M.; Garbuzova, I. A. J. Phys. Chem. B 1998, 102, 4918-4926.

3:40pm **BI-WeA6 Modification of Metal Oxide Surfaces for Biosensor and Biomaterial Applications Based on Assembled, Functionalized Poly(L-lysine)-g-poly(ethylene glycol)*, M. Textor*,** *J. Vörös, R. Hofer, D. Elbert,* ETH Zurich, Switzerland

Poly(L-lysine) grafted with poly(ethylene oxide) (PLL-g-PEG) is a polycationic block copolymer that spontaneously assembles as a monolayer at negatively charged metal oxide surfaces such as those formed by titanium oxide, tantalum oxide or niobium oxide. The interaction with the negatively charged surface is shown to be electrostatic through the terminal amine groups of the poly(L-lysine) side chains charged positively at pH below 9. The surfaces have been characterized ex situ using X-ray photoelectron spectrocopy, time-of-flight secondary ion mass spectrometry and reflection-absorption infrared spectroscopy. The planar optical waveguide (grating coupler) technique was used in situ both to monitor in real time the assembly process at the metal oxide waveguide surface, as well as to determine the degree of non-specific adsorption when exposed to serum. The degree of protein resistance was found to depend on the PLL-g-PEG coverage, on the grafting ratio between lysine monomer units and PEG side chains, and on the molecular weight of the PEG used. Using optimized polymer architectures, very low values of serum adsorption could be achieved, typically below the detection limit of our optical waveguide instrument (1 ng/cm2). The surfaces remain protein-resistant in flowing buffer solution at least up to 7 days. Functionalized PLL-g-PEG molecules were synthesized with functional groups such as biotin at the terminal position of the PEG side chains. The functionality of these polymer layers on optical waveguide chips was investigated using a model assay with streptavidin binding, followed by the adsorption of biotinylated recognition units and targeting of proteins such as IgG. This new polymeric interface is shown to have an excellent potential for future applications both in the area of bioaffinity sensor to control specific and non-specific adsorption and for implants such as stents.

4:00pm **BI-WeA7 Design and Characterization of Specific Biorecognition Interfaces using Derivatized Poly(L-lysine)-grafted-poly(ethylene glycol) Monolayers*, L.A. Ruiz-Taylor*,** *T.L. Martin, M. Heidecker, P. Indermuhle, P. Wagner,* Zyomyx, Inc.

Control of interfacial events such as specific recognition versus non-specific protein adsorption is a major issue in biotechnological applications. In diagnostic assays or biomaterial devices, non-specific binding events can often be the limiting factor towards higher detection sensitivity or implant integration, respectively. In this study, we report the design of interfacial polymers that have the ability to spontaneously adsorb to negatively charged surfaces under physiological pH and efficiently repel non-specific protein adsorption while providing PEG tethered functional/active sites for specific biomolecule recognition. As a model system, we synthesized biotin-derivatized poly(L-lysine)-grafted-poly(ethylene glycol) copolymers, PLL-g-(PEG)(1-x)(PEG-biotin)x, where x varies from 0.1 to 1. XPS was used to characterize the properties and the organization of the monolayers formed on titanium dioxide. Molecular recognition properties were investigated using radiolabelled streptavidin alone and within complex protein mixtures. We showed that the system allows the specific recognition of streptavidin, that the extent of the recognition is not influenced by the presence of other proteins and that streptavidin-horseradish peroxidase displays enzymatic activity on the modified surfaces. Finally, we used the PLLPEG-biotin copolymer system in conjunction with microfluidic patterning techniques to provide micron-size features with specific protein recognition separated by areas preventing non-specific binding, as shown by AFM and fluorescence microscopy.

4:20pm **BI-WeA8 Analysis of Protein Absorption on PEG-covered Silica Surfaces by ATR-FTIR***, N.A. Alcantar,* ***A. Stacy****, J. Au,* University of California, Santa Barbara*; T.L. Kuhl,* University of California, Davis*; E.S. Aydil, J.N. Israelachvili,* University of California, Santa Barbara

The most desirable characteristic of biomaterials is their capability to reject protein adhesion because non-specific adsorption of proteins to a surface of an artificial material enhances atypical development of cells. Surfaces covered with polyethylene glycol (PEG, OH-(CH@sub 2@-CH@sub 2@-O)@sub n@-H) have been shown to enhance protein rejection, nonimmunogenecity and nonantigenicity. In order to produce a generic biocompatible surface coating, we developed and analyzed a direct method for grafting PEG onto amorphous water plasma activated silica surfaces or films. In this paper, we investigated the biocompatibility of this PEG coating by measuring its ability to resist protein adsorption with attenuated total internal reflection Fourier transform infrared (ATR-FTIR) spectroscopy. PEG-coated silica surfaces, water plasma treated silica surfaces, and bare silica films were all exposed to several concentration solutions of fibrinogen and human serum albumin (HSA) at 37°C and pH=7.4 (imitating physiological conditions). We measured the protein adhesion to each of these three surfaces. We found that the surface covered with PEG had very little protein adsorption. Conversely, the bare silica surface has relatively high amounts of adsorbed protein. The surface treated with water plasma (but no polymer) adsorbed some proteins falling in between the bare silica and PEG-coated surfaces. PEG-covered silica coatings can be applied to protect diverse materials having different chemistries and shapes.

4:40pm **BI-WeA9 Combining Polymer Chemistry and Photolithography to Manipulate Gene Expression and Protein Synthesis***,* ***K.E. Healy,*** University of California, Berkeley, U.S.A*; J.H. Collier, C.H. Thomas,* Northwestern University*; C. Sfeir,* OHSU*; S.L. Golledge, D.G. Castner,* University of Washington

Materials that actively regulate the response of mammalian cells are designed to act via a combination of biomolecular recognition processes and device microarchitecture. We have developed methods that incorporate photolithography, organosilane chemistry, photoinitiated polymerization, and peptide chemistry to create surfaces that control the spatial distribution, projected area, and nuclear shape of mammalian cells. Interfacial interpenetrating polymer networks (IPNs) were synthesized by sequential photoinitiated free-radical polymerization of a thin layer of polyacrylamide followed by a secondary photoinitiation step using poly(ethylene glycol)-based monomers to create the network. Characterization of the IPNs by contact angle goniometry, spectroscopic ellipsometry, XPS, and static SIMS has confirmed the formation of an interfacial IPN ~ 20nm thick. These IPNs prevent protein adsorption and cell adhesion and therefore represent an excellent surface to control the spatial distribution of either biological macromolecules, cells, or viruses. In one application, materials with patterned surface chemistry could serve as templates for the organization of tissue structure surrounding medical devices, which would theoretically influence their biocompatibility. To address this hypothesis, the nuclear shape of mammalian cells was controlled on microfabricated substrata with reigospecific chemistry. Protein synthesis and expression at the mRNA level and were altered by changing the shape of the cell nucleus. Our data supports the concept of “architectural” transcription factors that promote gene expression based on optimal stress within the nuclear matrix transduced by the cytoskeleton.

5:00pm **BI-WeA10 Investigation of Protein Interactions with Poly (Ethylene Glycol) Modified Liposomes***,* ***J.L. Brash****, M.E. Price,* McMaster University, Canada

Liposomes have considerable potential as drug delivery vehicles. However unmodified liposomes are rapidly removed from the circulation by the reticuloendothelial system. This is believed to be initiated by adsorption of plasma proteins. Modification of liposomes with poly(ethylene glycol) (PEG) has been shown to increase their lifetime in vivo. Although there is some information on protein interactions with conventional liposomes, there is little if any on PEG-modified liposomes. In this study liposome interactions with fibrinogen in buffer and with plasma have been investigated. Sucrose-loaded large unilamellar liposomes were prepared. Dry phospholipid films (unmodified or modified with phosphatidylethanolamine-conjugated PEG (PE-PEG)) were hydrated with sucrose buffer followed by extrusion through two stacked 100 nm polycarbonate membranes. Liposome size distribution was estimated by dynamic light scattering (DLS) with diameters in the range of 135 ± 8 nm. Liposomes were incubated for 3 h in Tris-buffered 125I-fibrinogen solutions. The mixtures were centrifuged and the radioactivity of liposome pellet determined. Liposomes were also incubated in plasma and bound proteins identified by SDS solubilization followed by gel electrophoresis and immunoblotting using antibodies to some 20 plasma proteins. Fibrinogen adsorption was found to increase as solution concentration increased, with no apparent plateau. Adsorbed amounts decreased with incorporation of PEG and with increasing MW of PEG in the range 500-5000. The gels and immunoblots showed that the unmodified and PEG-modified liposomes adsorbed most of the proteins probed for. The protein patterns (relative amounts of each, degradation, activation) were similar.

Dielectrics
Room 312 - Session DI+EL+MS-WeA
Alternate Gate Dielectrics

Moderator: R. Ramesh, University of Maryland

2:00pm **DI+EL+MS-WeA1 Materials Considerations for High-K Gate Dielectrics for Scaled CMOS***,* ***G.D. Wilk,*** Lucent Technologies*; R.M. Wallace,* University of North Texas **INVITED**

Many materials systems are currently under consideration as potential replacements for SiO@sub 2@ as the gate dielectric material for sub-0.13 µm CMOS technology. A systematic consideration of the required properties of gate dielectrics, however, indicates that the key issues for selecting a high-k dielectric are permittivity and band offset, thermodynamic stability, crystal structure, and compatibility with the current or expected materials to be used in processing for CMOS devices. Many dielectrics satisfy some of these criteria, but very few materials actually satisfy all. A review of current work and literature in the area of high-k gate dielectrics is given, and some conclusions are drawn for various systems based on reported results and fundamental materials considerations.

2:40pm **DI+EL+MS-WeA3 New High k Thin Films with Improved Physical and Electrical Properties***,* ***Y. Kuo****, J. Donnelly, J. Tewg,* Texas A&M University

When the minimum device dimension is shrunk to 100 nm, the conventional silicon oxide cannot fulfill many requirements of the device.@footnote 1@ For example, the thin gate dielectric layer (e.g., < 1.2 nm) will have a high leakage current and cannot stop the boron penetration. The dielectric constant of silicon oxide (e.g., 4.0) is too low for the small-size storage capacitor cell. Therefore, it is urgent to develop a new kind of thin film dielectric that has a high dielectric constant (high k) and can satisfy all stringent material, process, and device requirements. Metal oxides are ideal candidates for the gate dielectric application because their compositions are simple and their k values are high enough to last for next several generations of devices. In addition to the high interface states, a metal oxide has the problem of high leakage current, which is caused by the polycrystalline phase formation during the high temperature process.@footnote 2,3@ In this paper, we present new results on high k metal oxides that have high amorphous-to-polycrystalline transition temperatures. By adding a third element into tantalum oxide, e.g., Ti, Cu, and Mo, the film can exist in the amorphous phase in an extended temperature range. The leakage current at a high temperature is lowered. Material and electrical characteristics of the new film, e.g., by x-ray diffraction, ellipsometer, current-voltage and capacity-voltage curves, will be shown and discussed. The influence of the deposition process, i.e., reactive co-sputtering, to film properties will also be presented. These new high k dielectrics have the potential of being used as gate dielectrics in future MOS devices. @FootnoteText@ @footnote 1@ International Technology Roadmap for Semiconductors, 1999 ed., SIA, etc. @footnote 2@ S. R. Jeon, S. W. Han, and J. W. Park, J. Appl. Phys. 77, 5978, 1995.

@footnote 3@ R. B. van Dover, R. M. Fleming, L. F. Schneemeyer, G. B. Alers, and D. J. Werder, IEDM, 823, 1998.

3:00pm **DI+EL+MS-WeA4 Chemical and Microstructural Separation of Homogeneous Plasma Deposited (ZrO@sub2@)@subx@(SiO@sub2@)@sub(1-x)@ films (x @<=@ 0.5) into SiO@sub2@ and ZrO@sub2@ Phases after Rapid Thermal Annealing in Ar at 900°C**, ***B. Rayner***, *R. Therrien, G. Lucovsky,* North Carolina State University

Zr-silicate alloys along the pseudo-binary join from SiO@sub2@ to ZrO@sub2@ have attracted interest as high-k dielectrics for Si CMOS devices with equivalent oxide thickness extending to 0.6 nm. In this study alloy films were deposited on HF-last and pre-oxidized and/or nitridized Si(100) by remote plasma enhanced chemical vapor deposition using Zr(IV)-t-butoxide. Film and interface chemical composition, local atomic bonding, and film morphology were studied by Auger electron spectroscopy, Fourier transform infrared absorption, X-ray diffraction, and Rutherford back-scattering. These studies identified two alloy regimes: (i) SiO@sub2@-rich compositions to the compound silicate, ZrSiO@sub4@ (x = 0.5), where properties may be suitable for high-k applications, e.g., films are amorphous on deposition and remain so up to at least 800°C, and (ii) ZrO@sub2@-rich compositions in which films are either partially or totally crystalline on deposition, or after relatively low temperature (< 600°C) anneals. Alloys in the SiO@sub2@-rich regime are chemically-ordered as-deposited at ~350°C with predominantly Si-O-Si and Zr-O-Si bonds, but after annealing in Ar at 900°C for 60 s, separate chemically and microstructurally into SiO@sub2@ and ZrO@sub2@ phases. The ZrO@sub2@ phase is crystalline at the ZrSiO@sub4@ composition. This separation may limit integration of these films into devices which incorporate polycrystlline-Si gate electrodes requiring dopant activation at temperatures > 900°C. Capacitance-voltage and current-voltage characteristics will be presented for as-deposited and annealed films to illustrate the effects of chemical phase separation and crystallization in defining maximum post deposition processing temperatures.

3:20pm **DI+EL+MS-WeA5 A Study of ZrO@sub2@ and Zr-silicate Thin Film for Gate Oxide Applications**, ***S.-W. Nam***, Yonsei University & Samsung Electronics Co., Korea; *J.-H. Yoo, H.-Y. Kim, D.-H. Ko,* Yonsei University, Korea; *S.-H. Oh, C.-G. Park,* Pohang University of Science and Technology (POSTECH), Korea; *H.-J. Lee,* Stanford University

We investigated the microstructures and electrical properties of ZrO@sub2@ and Zr-silicate thin films deposited by reactive DC magnetron sputtering on Si substrate for gate dielectric application. The films deposited on Si with various deposition conditions and annealing treatments were analyzed by spectroscopic elipsometry, XRD, AFM and XPS. The refractive index of the ZrO@sub2@ thin films increased upon annealing. The ZrO@sub2@ film deposited at low temperature and low power showed amorphous structure, which the films deposited at high temperature and high power showed crystalline structures. The growth of the interfacial oxide between ZrO@sub2@(or Zr-silicate) and Si substrate was observed by cross sectional HR-TEM. C-V and I-V measurements of the MOSCAP structures showed that the accumulation capacitance value and the leakage current level decreased upon annealing in O@sub2@ gas ambient, which is explained by the formation of the interfacial SiO@sub2@ layer.

3:40pm **DI+EL+MS-WeA6 Ultra-thin Zirconium Oxide Films Deposited by Rapid Thermal CVD for MOSFET Applications**, ***Y. Lin,*** *J.P. Chang,* University of California, Los Angeles

The increasingly tighter process specifications for the next generation microelectronic devices dictate the usage of metal oxides such as zirconium oxide as insulators for better process control and a more reliable dielectric/silicon interface.@footnote 1@ Zirconium t-butoxide is used with O@sub 2@ in this work to deposit zirconium oxide in a RTCVD system. The deposition temperature can be rapidly ramped to and controlled at 400-600°C, and the physical properties of the ZrO@sub 2@ films are characterized by XPS, XRD, AFM, TEM, and spectroscopic ellipsometry to determine the film compositions, chemical states, film microstructures, morphology, thickness, and index of refraction. Amorphous and nearly stoichiometric ZrO@sub 2@ has been deposited with less than 0.2nm variation in thickness across a 4" wafer. The dielectric constant is 3-4 times greater than that of SiO@sub 2@. Leakage current of a ZrO@sub 2@ film with an effective oxide thickness of 10 Å is three orders of magnitude lower than that of a 10Å thermal SiO@sub 2@ film. Post-deposition annealing at 500-700°C is shown to be effective in removing the majority of the incorporated carbon and further reduce the leakage current. However, there exists an optimal carbon doping level where carbon effectively passivates the electrically active defects and reduces the leakage current. We propose a simple kinetic model to describe the heterogeneous reactions responsible for the film deposition. NMOS transistors are fabricated and tested to determine the dielectric constant, leakage current, I-V and C-V characteristics of the zirconium oxide films. Moreover, stress induced leakage current and time dependent dielectric breakdown will also be detailed to assess the material reliability for its applications in microelectronics. @FootnoteText@ @footnote 1@G. D. Wilk, and R. M. Wallace, "Electrical properties of hafnium silicate gate dielectrics deposited directly on silicon," Appl. Phys. Lett., 74(19), 2854(1999).

4:00pm **DI+EL+MS-WeA7 High-quality Ultrathin Fluorinated Silicon Nitride Gate Dielectric Films Prepared by Plasma Enhanced Chemical Vapor Deposition Employing NH@sub 3@ and SiF@sub 4@**, ***H. Ohta***, *M. Hori, T. Goto,* Nagoya University, Japan

The silicon nitride (SiN@sub x@) film attracts much attention as scaled gate dielectric films in next generation@super ,@s ULSI. However, the conventional SiN@sub x@ film has a poor interface with silicon and is leaky due to a high trap density in the film. Recently, we have developed ultrathin fluorinated SiN@sub x@ films formed by ECR-PECVD employing NH@sub 3@/SiF@sub 4@. It is known that the average bond energy (5.73eV) of Si-F is higher than that of Si-H (3.18eV). Therefore, it is expected that the Si-F bond in the film should have improved the quality of gate dielectric film. In this study, we have investigated properties of ultrathin SiN@sub x@ films (4nm) formed at 350°C. These films (fluorinated SiN@sub x@ films) contain fewer hydrogen atoms than the conventional SiN@sub x@ films formed by ECR-PECVD employing NH@sub 3@/SiH@sub 4@. As-deposited fluorinated SiN@sub x@ films indicated the excellent hysteresis loop (20mV) in the C-V curve, and reduced the leakage current by several orders of magnitude than the thermal SiO@sub 2@ in the identical equivalent oxide thickness (EOT). These film properties and the surface reactions for the SiN@sub x@ film formation with good quality are discussed on the basis of results of the in-situ XPS, in-situ FT-IR RAS, FT-IR, and thermal desorption mass spectroscopy (TDS). As a result, the control of fluorine concentration in the SiN@sub x@ films was found to be a key factor for forming the fluorinated SiN@sub x@ films with high quality at low temperatures. The fluorinated SiN@sub x@ is very effective for ultrathin gate dielectric films in next generation@super ,@s ULSI.

4:20pm **DI+EL+MS-WeA8 Elimination of Carbon Impurities in the Metalorganic Chemical Vapor Deposition (MOCVD) of Titanium Dioxide on Silicon**, ***M. Yoon***, *A.C. Tuan, V.K. Medvedev,* University of Washington; *J.W. Rogers, Jr.,* Pacific Northwest National Laboratory

A novel process has been developed for the deposition of titanium dioxide thin films on p-type Si(100) with high quality interfacial characteristics and the absence of carbon. Elimination of carbon contaminants in the titanium dioxide film and at the interface between the oxide and silicon is important because the presence of impurities can severely degrade the electrical properties of the device. This novel process consists of three stages of deposition in an ultra-high vacuum chamber. Initially, a continuous titanium layer is deposited on silicon using a titanium sublimator. This titanium layer is then oxidized using a gas phase oxygen source to form a TiO@sub x@ buffer layer. Subsequently, a titanium dioxide thin film is deposited by MOCVD using titanium tetrakis-isopropoxide (TTIP) at low temperature (below 650K). Auger electron spectroscopy (AES) analysis at each stage of growth shows no evidence of carbon contamination either within the titanium dioxide layer or at the TiO@sub 2@/Si interface. Additional AES measurements suggest that the titanium layer grows on silicon according to the Stranski-Krastanov mode, which permits uniform growth. A carbon-free titanium dioxide thin film was successfully deposited on silicon using this novel process.

4:40pm **DI+EL+MS-WeA9 Microscopic Understanding of the Interface for the Heteroepitaxy of Crystalline Oxides on Silicon**, ***S. Gan***, *D.E. McCready, D.J. Gaspar, Y. Liang,* Pacific Northwest National Laboratory

With SiO@sub 2@ approaching its fundamental limit as the gate dielectric in the existing Si-based CMOS technology, searching for alternative gate oxides with high dielectric constants is crucial for the next generation of devices. Recent work showed crystalline oxides such as SrTiO@sub 3@ (STO) is promising as an alternative to SiO@sub 2@ in MOS capacitors. One of the most important issues is how to integrate it into the existing Si-based technology, the first step of which is the growth of epitaxial oxides on Si substrates. Here we present our recent results on the study of the oxide-silicon interface, which plays a critical role in growing high-quality STO films. Employing scanning tunneling microscopy (STM), x-ray photoelectron spectroscopy (XPS), low-energy electron diffraction (LEED), we characterized the interfacial structure of each template layer (Sr and SrO) grown on Si in situ. The results revealed that the strontium covered silicon surfaces exhibit a series of reconstructions, including a (2x1) structure that provides the most stable interface for the growth of oxides. In addition, we used time-of-flight second ion mass spectrometry (TOF-SIMS) and x-ray diffraction (XRD) to investigate the interfacial chemistry and film structure. By combining these techniques, we correlated the interface structures with film properties, which allowed us to identify suitable interfacial templates for optimized growth. @FootnoteText@ Pacific Northwest Laboratory is a multiprogram national laboratory operated by Battelle Memorial Institute for the U.S. Department of Energy under Contract DE-AC06-76RLO 1830.

5:00pm **DI+EL+MS-WeA10 Formation of Ultrathin Yttrium Silicate by Thermal Oxidation of Yttrium on Silicon*, M.J. Kelly*,** *J.J. Chambers, D. Niu, G.N. Parsons,* North Carolina State University

We show that direct thermal oxidation can be used to form thin (<50@Ao@) high-k metal silicate layers directly on crystalline silicon. Bulk thermodynamics indicates that several high-k metal oxides (including oxides of Hf, Zr, Al, Y, La, etc.) will be stable with respect to silicon dioxide formation when the oxide is in contact with silicon. However, most low temperature approaches (PVD, CVD, or MBE) for metal oxide deposition on silicon involve elementary reaction steps that include metal-silicon bond formation before oxidation, resulting in uncontrolled interface layers between the metal oxide and silicon. We can utilize this mechanism to form yttrium silicate films on silicon by first sputtering thin (<10@Ao@) metal films on silicon, vacuum annealing at 300-600Â°C to form a silicide, then oxidizing at 600-900Â°C. XPS, medium energy ion scattering, and IR indicate film composition is close to yttrium orthosilicate (Y2O3Â·SiO2) with some excess Y2O3, depending on anneal conditions. Oxidation kinetics (determined from thicknesses measured by TEM) indicate an initial fast oxidation rate (due to oxidation of metal silicide), followed by a slower process (due to oxidation of underlying silicon). CV analysis of 42@Ao@ films show oxide equivalent thickness ~12@Ao@, consistent with dielectric constant ~14. Leakage is <1A/cm2 at 1V in accumulation. IR and XPS indicate that films do not phase separate when annealed up to 900Â°C for 20 minutes. Thin (<10@Ao@) silicon oxide and nitride interface layers have been formed in-situ by remote plasma exposure before metal deposition and their effect on interface reaction kinetics have been analyzed by XPS and MEIS. Interfacial oxide is observed to have a negligible effect on interface reactions, but results suggest interface nitrogen tends to block silicide formation before oxidation. These results give important insight into controlling interface structure for implementing high-k materials into silicon devices.

Magnetic Interfaces and Nanostructures
Room 206 - Session MI+EL-WeA

Magnetic Semiconductors and Hybrid Structures II

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

2:00pm **MI+EL-WeA1 Spin-dependent Behavior in Magnetic / Semiconductor Heterostructures*, B.T. Jonker*,** Naval Research Laboratory

INVITED

Magnetic / semiconductor heterostructures offer many exciting opportunities for spintronic applications, ranging from hybrid device structures to direct spin injection. We describe here recent results of each. We have fabricated hybrid logic cells which provide fully reprogrammable, nonvolatile logic operation by combining GMR elements with InAs/AlSb/GaSb resonant interband tunneling diodes (RITDs). Such programmable cells allow the use of a low component count common building block for multiple logic functions, and combine the low power, high speed operation of the RITD with the nonvolatile character of GMR elements. Electrical spin injection and transport in semiconductors is another promising avenue to add spin-dependent functionality to the many attractive device properties of semiconductor compounds -- it provides a very simple means of spin injection, and significantly broadens the potential for practical applications.@footnote 1-3@ We have recently demonstrated highly efficient electrical injection of spin-polarized electrons into a AlGaAs/GaAs-based quantum well LED heterostructure using a non-lattice matched epilayer of the semimagnetic semiconductor ZnMnSe as the spin injecting contact. The electroluminescence (EL) from the quantum well is strongly polarized, and provides a quantitative measure of spin injection across the ZnMnSe/AlGaAs interface. Other components of the EL spectrum exhibit little polarization, and provide insight into spin relaxation mechanisms. Ferromagnetic semiconductors provide an ideal contact for electrical spin injection and/or transport -- they are closely matched in conductivity and band structure, and require no large magnetic bias field to produce spin polarized carriers. Several candidate materials will be discussed. ** Supported by ONR and the DARPA SPINS program.@FootnoteText@ @footnote 1@ B.T. Jonker et al, submitted. @footnote 2@ R. Fiederling et al, Nature 402, 787 (1999) @footnote 3@ Y. Ohno et al, ibid p. 790.

2:40pm **MI+EL-WeA3 MBE Growth of Ni@sub 2@MnIn/InAs (001) Heterostructure*, J.Q. Xie*[1],** *J.W. Dong, L.C. Chen, J. Lu, C.J. Palmstrom,* University of Minnesota

InAs is the semiconductor of choice for spintronic applications due to the ease of forming ohmic contacts and its high electron mobility. The former arises from the fact that the Fermi level tends to be pinned in the conduction band at the metal/InAs interface. Although no elemental ferromagnetic metals are lattice matched to InAs, Ni@sub 2@MnIn is nearly lattice matched. In the bulk, stoichiometric Ni@sub 2@MnIn is ferromagnetic at room temperature and has the cubic L2@sub 1@ Heusler structure with a lattice parameter 0.2% larger than that of InAs. In this talk, we report on the growth of ferromagnetic Ni@sub 2@MnIn films on (001) InAs by molecular beam epitaxy (MBE). Both in situ reflection high energy electron diffraction and ex situ X-ray diffraction measurements indicate that Ni@sub 2@MnIn films grow epitaxially on MBE-grown (001) InAs substrates. Vibrating sample magnetometer and superconducting quantum interference device magnetometer measurements show that the deposited films are ferromagnetic with a Curie temperature ~300 K. Our initial results indicate that Ni@sub 2@MnIn grows in a hexagonal Ni@sub 2@In@sub 3@-type structure, which probably results from either interfacial chemistry or composition. In this talk, the effects of interfacial layers on the growth, structure and magnetic properties of Ni@sub 2@MnIn thin films will be discussed.

3:00pm **MI+EL-WeA4 Investigation of the Microstructural Dependence of Magnetic Properties for MnSb/Bi Multilayers Grown on Sapphire*, M.L. Reed*,** *H.H. Stadelmaier, N.A. El-Masry,* North Carolina State University

The microstructural dependence of the magnetic properties for MnSb/Bi multilayer films grown on sapphire substrates by pulsed laser deposition were investigated by X-ray diffraction(XRD), vibrating sample magnetometer (VSM), and magnetoresistance measurements. Typical hysteresis loops for the MnSb/Bi multilayers are characteristic of ferromagnetic materials. However, altering the growth parameters produces a second coercive field indicating the formation of a second magnetic phase. XRD analysis identified the presence of a peak centered between (0002)MnSb and (0002) MnSb, which in previous samples had not been observed. A change in the relative planar Hall resistance from 1% to 16% with applied magnetic field was also observed in the films that exhibit this second phase. We discuss the nature of this phase and its effect on the magnetic properties of MnSb/Bi.

3:20pm **MI+EL-WeA5 Ferromagnetic Fe/Ag-GaAs Waveguide Structures for Wideband Microwave Notch Filter Devices*, W. Wu,*** University of California, Irvine*; C.S. Tsai,* University of California, Irvine and Academia Sinica, Taiwan*; C.C. Lee, H.J. Yoo, J. Su,* University of California, Irvine

Ferromagnetic Fe/Ag thin films were epitaxially grown on GaAs substrate by molecule beam epitaxy (MBE) system. Magneto-optic kerr effect (MOKE) experiment was used to measure the magnetization and sample magnetic anisotropy. Ferromagnetic resonance (FMR) peak-to-peak linewidths @delta@H@sub pp@ are identified with the narrowest linewidth of 23 Oe. Wideband electronically tunable microwave band-stop filters were successfully fabricated utilizing both the flip-chip and the integrated configurations, using Fe/Ag-GaAs waveguide structures. The coupling between the microwave signal and the spin excitations happened in ferromagnetic Fe films. Maximum coupling and thus strong attenuation of the microwave power occur at the FMR frequency of Fe, as determined by the applied magnetic fields. A frequency tuning range of 10.6 to 27.0 GHz has been measured with the flip-chip type filter. For the integrated type filter, a tuning range as large as 10.7 to 36 GHz for the peak absorption carrier frequency of a propagating microwave has been accomplished by varying a magnetic field from 0 to 4,600 Oe. Our studies show that Fe/Ag-GaAs waveguide structure is a very promising system for use in future microwave magnetoelectronics as they have well-defined magnetic properties, as well as favorable electrical properties.

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[1] **Falicov Student Award Finalist**

3:40pm **MI+EL-WeA6 Non-Volatile Reprogrammable Logic Elements using a Hybrid RTD-GMR Circuit@footnote 1@*, A.T. Hanbicki,*** *R. Magno, S.-F. Cheng,* Naval Research Laboratory*; J.E. Mattson,* Naval Research Laboratory, US*; Y.D. Park, A.S. Bracker, B.R. Bennett, B.T. Jonker,* Naval Research Laboratory

Programmable logic devices and gate arrays are increasingly important in new computation and digital logic systems. The resonant tunneling diode (RTD) is an especially attractive device component for such applications because it offers high frequency and low power operation due to its unique IV characteristics. It has been shown that memory, multi-value logic and monostable-bistable logic elements (MOBILE)@footnote 2@ can be constructed using RTDs and FETs. We describe here the fabrication and operation of programmable gates and logic cells based on the combination of RTDs with magnetic elements, yielding fully reprogrammable, nonvolatile functions. The circuits discussed are constructed with resonant interband tunneling diodes (RITD) combined with giant magneto-resistance (GMR) elements. The RITDs are fabricated from MBE-grown InAs/AlSb/GaSb/AlSb resonant tunneling structures using standard processing techniques, and provide a peak current of 1.4 x 10@super 4@ A/cm@super 2@. The GMR elements consist of Co/Cu multilayers, and exhibit a value of @DELTA@R/R = 28% at 300 K (CIP). Simple series and parallel circuit combinations demonstrate continuous or 2-state tunability of the RITD I-V characteristic. Threshold detection is demonstrated, for the RITD and GMR in series, by ramping the magnetic field. With the elements we have chosen, the output can be switched by 0.5 V. MOBILE-like inverter operation is observed in a GMR/2-RITD circuit. Specifics of several other circuits will also be discussed. Work is in progress to fabricate an on-chip GMR/RITD integrated circuit. @FootnoteText@ @footnote 1@This work was supported by the Office of Naval Research. @footnote 2@K. Maezawa and T. Mizutani, Jpn. J. Appl. Phys., 32 (1993) L42.

4:00pm **MI+EL-WeA7 Magnetization-Controlled Resonant Tunneling in Magnetic Heterostructures***, D.O. Demchenko, A.N. Chantis,* ***A.G. Petukhov***, South Dakota School of Mines and Technology

Recent advances in molecular beam epitaxial growth made it possible to fabricate exotic heterostructures comprised of magnetic films or buried layers (ErAs, Ga@sub x@Mn@sub 1-x@As) integrated with conventional semiconductors (GaAs) and to explore quantum transport in these heterostructures.@footnote 1,2@ It is particularly interesting to study spin-dependent resonant tunneling in double-barrier resonant tunneling diodes (RTD) with magnetic elements such as GaAs/AlAs/ErAs/AlAs/GaAs, Ga@sub x@Mn@sub 1-x@As/AlAs/GaAs/AlAs/GaAs, and GaAs/AlAs/Ga@sub x@Mn@sub 1-x@As/AlAs/GaAs. We present the results of our theoretical studies and computer simulations of transmission coefficients and current-voltage characteristics of resonant tunneling diodes based on these double-barrier structures. Interband resonant tunneling of electrons (ErAs-based RTDs) and resonant tunneling of holes (Ga@sub x@Mn@sub 1-x@As-based RTDs) is considered. Our approach is based on 8x8 k.p perturbation theory with exchange splitting and strain effects taken into account. We analyze Zeeman splittings of different resonant channels as a function of magnetization. We found that resonant tunneling I-V characteristics of the double-barrier magnetic heterostructures strongly depend on the doping level in the emitter as well as on the orientation of the magnetization. The peculiarities spin-dependent tunneling in GaAs/ErAs- and GaAs/GaMnAs-based heterostructures are explained in terms of strong interaction of confined hole states with magnetization, spin-orbit interaction and angular momentum selection rules. @FootnoteText@ @footnote 1@ D. E. Brehmer, K. Zhang, C. J. Schwartz, S. P. Chau, and S. J. Allen, Appl. Phys. Lett. 67, 1268 (1995). @footnote 2@ H. Ohno, N. Akiba, F. Matsukura, K. Ohtani, A. Shen, and Y. Ohno, Appl. Phys. Lett. 73, 363 (1998).

MEMS
Room 309 - Session MM-WeA
MEMS Processing

Moderator: W.D. Cowan, Air Force Research Laboratory

2:00pm **MM-WeA1 Surface Micromachining - Process Modeling***,* ***C.C. Wong****, P. Ho,* Sandia National Laboratories*; R.W. Walker,* Los Alamos National Laboratory*; R.P. Pawlowski,* Sandia National Laboratories

Advances in microsystem technology are allowing increasingly complex micro-structures to be built. The ability to visualize structures during the design phase is becoming correspondingly more important. Surface micromachining involves multiple deposition (CVD) and etching (plasma or wet) steps, and each step can introduce non-idealities to the geometry of the structure. Virtual prototyping can speed the design process and reduce the time lost when flaws are discovered during fabrication. Predicting the true dimensions of the final product requires that the effects of the manufacturing processes be modeled accurately. At Sandia, we are developing detailed "physics-based" models to generate the correct shape of micro-features. A modular approach examines the various processes used in device fabrication, and separates the disparate length scales in the fabrication processes. The initial studies investigate the low pressure CVD of polysilicon from silane, which deposits the structural Si material. First, models of the process reactor, MPSalsa (3D) and OvenD (two coupled 1D models), analyze the reacting flows in the multi-wafer furnace. Using a published silane mechanism, the predicted deposition rates for the standard conditions agree with experiment (within 15%). Results from the reactor-scale models are then used as boundary conditions for feature-scale models of the time-dependent evolution of the polysilicon. Simulations using TopoSim3D reproduce the observed conformal deposition. Wet-etch processes to remove sacrificial oxide layers are also being studied. Preliminary analyses using the 3-D GOMA code give reasonable agreement between experiment and the predicted position of the advancing etch front.

2:20pm **MM-WeA2 Application of Magnetic Neutral Loop Discharge Plasma in Deep Silica Etching***,* ***W. Chen,*** ULVAC JAPAN, Ltd., Japan*; K. Sugita,* ULVAC JAPAN, Ltd.*; T. Hayashi,* ULVAC JAPAN, Ltd., Japan*; T. Uchida,* ULVAC JAPAN, Ltd.

Generally, plasma density is well known to be concerned with etch rate, and electron temperature is a key parameter for the decomposition of reactive gases which is also relative to the operating pressure. So, margin of plasma production in process can be defined as the highest density, lowest applicable electron temperature and pressure, which indicate the variability of gas chemistry for processes. Process pressure is an especially important parameter for the Micro-Electro-Mechanical-Systems (MEMS). Metal mask and/or doped glass are usually used. These metal masks, such as Cr, Ni and WSi, and doped materials do not reactive to the dominant reactive species of CF@sub x@, which are consumed by physical sputtering mainly. Certainly, the sputtered clusters are easily re-deposited to sample substrate by collision of the sputtered metal cluster with neutral gases in high-pressure process, which may result in a rough surface and large taper angle. Magnetic neutral loop discharge (NLD) plasma@Footnote 1-3@ is a wide marginal one with a high density (>10@sup 11@ cm@sup -3@) and low electron temperature of about 2.5eV in a very low pressure of about 0.2Pa. Using NLD system, vertical trench structures for optical wave-guide were successfully fabricated on fused quartz glass and silica film with very smooth surface in the depth of 6-30mm. Meanwhile, the etch rate were kept greater than 500nm/min with good uniformity (deviation of @sigma@

2:40pm **MM-WeA3 Application of Deep Silicon Etching and Wafer Bonding in the MicroManufacturing of Turbochargers and Micro Gas Turbine Engines***,* ***A.A. Ayon****, J. Protz, R. Khanna, X. Zhang, A. Epstein,* Massachusetts Institute of Technology **INVITED**

This paper describes the first successful micromanufacturing of MEMS turbochargers and micro gas turbine engines (MGTE), complete with an integrated compressor, turbine, and combustor. The realization of both devices involves the deep etching and fusion bonding of six single-crystal silicon wafers. The deep etching steps define turbomachinery and gas bearings, associated with the rotor, as well as fluidic interconnects and instrumentation access ports. A turbocharger includes a freely rotating rotor comprised of a turbine and a compressor mounted on the same shaft. It increases the power output of the engine to which it is attached by effectively acting as a pump to force more fuel into the engine. With this scheme, the turbine extracts power from the hot exhaust gas stream to drive the compressor that, in turn, raises the fluid density, and, hence, the mass flow rate to the engine. Turbochargers have applications to conventional and rocket engines, fuel cells, and microfluidic systems. A MGTE integrates a combustor with the turbocharger, making the device a complete, self-powered engine, for propulsion and electrical power generation applications. For the fabrication of the MGTE, the turbocharger geometry was modified to include a cooling jacket that linked the compressor and turbine and that also surrounded a combustion chamber. This introduced additional challenges for the microfabrication of three of the six required wafers, due to the extensive removal of the underlying silicon substrate and the concomitant fragility of the wafers involved. Fully operational, the demonstration MGTE is expected to have a rotor spinning at the rate of 1.2 million rpm, burn 16 g/hour of H2 fuel and produce 11 g of thrust. The present work is applicable to projects with intricate geometries requiring stacks of bonded wafers. We describe and discuss the etching and bonding challenges, as well as observations and results obtained in the microfabrication of these heat engines.

3:20pm **MM-WeA5 MEMS Fabrication Technology Applied to Large Area X-ray Image-sensor Arrays***, **J.H. Daniel**, B. Krusor, R. Apte, R.A. Street,* Xerox Palo Alto Research Center*; A. Goredema, P. Kazmaier,* Xerox Research Center Canada

Micromachining has potential applications for large area image sensors and displays, but conventional MEMS technology, based on crystalline silicon wafers cannot be used. Instead, large area devices use deposited films on glass substrates. This presents many challenges for MEMS, both as regards materials for micro-machined structures and the integration with large area electronic devices. We are exploring the novel thick photoresist SU-8, as well as plating techniques for the fabrication of large area MEMS. As an example of its application, we have applied this MEMS technology to improve the performance of an amorphous silicon based image sensor array. SU-8 is explored as the structural material for the X-ray conversion screen and as a thick interlayer dielectric for the thin film readout electronics of the imager. Medical X-ray imagers have a thick (200-500 micron) layer of phosphor, which converts the X-rays into visible light, placed directly on top of the photodiodes. Spatial resolution is limited because of light scattering in the phosphor. In order to obtain the full resolution of the pixel array the phosphor layer needs to be micro-patterned into cells which collimate the generated light. This cell structure was patterned with a 300-400 micron thick layer of SU-8. The SU-8 cell walls need to be made reflective in order to prevent light from scattering into a neighboring cell which is achieved by sputtering a thin metal layer. Subsequently the cells are filled with a phosphor. A second application is the use of SU-8 as a thick interlayer dielectric to reduce noise due to capacitive coupling in the thin film electronic circuit of the imager. Nickel electroplating is used to metallize the deep contact vias. The compatibility of SU-8 with thin film deposition methods, such as amorphous silicon PECVD, will be discussed. Processing challenges which are particularly important for large area fabrication, will be addressed.

3:40pm **MM-WeA6 Switching of Interfacial Energies in Polymeric Coatings***, **B.C. Bunker**, J.G. Kushmerick, W.L. Smith, M.S. Kent,* Sandia National Laboratories*; G.P. Lopez,* University of New Mexico*; X.-Y. Zhu,* University of Minnesota*; D.L. Huber, T.D. Dunbar,* Sandia National Laboratories

Polymeric coatings are under investigation for controlled switching of interfacial energies in microanalytical systems. Switching of water contact angles using films of poly n-isopropylacrylamide (PNIPAM) is of interest for driving liquids in microchannels, while switching of polymer configurations within polyethylene oxide (PEO) films could control properties such as protein adsorption. Films of PNIPAM and PEO have been tethered to gold and silicon substrates. Thermal and electrical stimuli have then been applied to the films to try to induce inverse temperature transitions. Film behavior has been monitored using a combination of contact angle measurements and force-distance profiles obtained using an interfacial force microscope. Results show that below the phase transition, PEO films are hydrated, and are attractive to scanning probe tips. Above the transition, the water is removed and the attractive potential drops by an order of magnitude. Moving above and below the transition temperature in PNIPAM films can induce changes in the water contact angle of from 10° up to 60° depending on how the polymer is tethered to the surface. The number of switching cycles is also dependent on the nature of the polymer-substrate interface. Limited switching is sometimes associated with decomposition or desorption of the active polymer. Such decomposition is illustrated for the specific example of a short-chain PEO film (EG3) attached to gold via a thiol coupling agent.

4:00pm **MM-WeA7 A Novel Anti-Stiction Method Using the Harmonic Excitation on the Microstructure***, **W.P. Lai**, W. Fang,* National Tsing Hua University, Taiwan

The sticking problem due to the reaction mechanism between rinse liquid and microstructures becomes a serious issue in micromachining fabrication processes. A novel anti-stiction method using the harmonic excitation on the microstructure is presented in this research. The proposed method had been studied through the analytical and experimental approaches. Consequently, the yield of the micromachining processes can be significantly improved by this technique. We exploit a simplified model consisting of a single degree of freedom mass-spring-damper system to simulate the drying process of the microstructure. In this model, the equivalent spring effect mainly comes from the Laplace pressure@footnote 1@ of the liquid film and the equivalent damping effect @footnote 2@ is due to the squeeze@footnote 3@ of the liquid film. Based on the analysis, the dynamic response of the microstructure including the resonant frequency and the damping characteristic of the drying system were predicted. Analysis results displayed that the system is initially underdamped, then is critically damped, and finally is overdamped when the drying time increased. Hence the cantilever beam could be separated with the liquid film by the harmonic excitation at the underdamped condition. In application of the proposed anti-stiction technique, we fabricated silicon oxide cantilevers on (111) silicon wafer. The micromachined cantilever was 0.7 µm thick, 16 µm wide, and 120 µm long, and the gap between the beam and the substrate was 4 µm. The sample was excited by a PZT actuator at various frequencies. After excited by a 250 KHz harmonic load for 10~110 seconds, the beam was released from the substrate. However, the beams were sticking to the substrate permanently if they were not driven by the harmonic excitation. The application of this technique is also demonstrated by the experiment. Theoretical predictions of the dynamic behavior of microstructure during drying process agree well with experimental results. In short, the proposed technique effectively enhances yield rate of the microstructure without additional masks and complicated process. Although the application of the proposed approach is limited to the overdamped system, it provides an additional option to prevent stiction problem. @FootnoteText@@footnote 1@Takeshi Abe, W. C. Messner, and M. L. Reed, 'Effects of elevated temperature treatments in microstructure release procedures' Journal of Microelectromechanical System, vol. 4, pp. 66-74, 1995. @footnote 2@ H. Hosaka, K. Itao, and S. Kuroda, 'Damping characteristics of beam-shaped micro-oscillators' Sensors and Actuators A, vol. 49, pp. 87-95, 1995. @footnote 3@ J. J. Blech 'On isothermal squeeze films' ASME Journal of Lubrication Technology, vol. 105, pp. 615-620, 1983.

4:20pm **MM-WeA8 Control of Residual Stress in Thick Sputtered Metal Films***, **J.M. Melzak**, D.A. Greer,* Case Western Reserve University*; S. Rajgopal, K.S. Lebouitz,* XACTIX, Inc.*; M. Mehregany,* Case Western Reserve University

Metals are the structural material of choice for a growing number of MEMS applications (e.g., optical elements, relays) because of their high reflectivity and low resistivity. This paper investigates the relationship between the parameters used to deposit such thick (1µm) films by DC magnetron sputtering and the resulting residual stress values. The materials of interest-aluminum, tungsten, and a ternary alloy of aluminum/silicon/copper-exhibit quite different residual stresses for a given set of deposition parameters, as well as reacting quite differently to changes in deposition parameters. For example, 1µm-thick tungsten films deposited on silicon at a pressure of 5 mTorr exhibit a compressive stress of 253 MPa while aluminum films deposited under the same conditions have a tensile stress of 73 MPa. Increasing the deposition pressure to 15 mTorr results in a highly tensile tungsten film, whereas the effect on aluminum's residual stress is minimal. As-deposited thick films of these materials have been characterized using wafer curvature, surface profilometry, and TEM analysis. Furthermore, a one-mask surface micromachining process that selectively etches the underlying silicon with xenon difluoride (XeF@sub 2@) has been used to fabricate metal cantilever beams, in order to qualitatively examine residual stress gradient.

4:40pm **MM-WeA9 SiC Surface Micromachining Process Development and Device Characterization***, **J.D. Scofield**, B.N. Ganguly,* Air Force Research Laboratory*; A.J. Steckl,* University of Cincinnati

TA silicon carbide surface micromaching process has been developed for the fabrication of robust MEMS structures. A direct etch and release procedure has been demonstrated using both Silicon dioxide and poly-silicon sacrificial layers. Cubic silicon carbide films were grown and characterized on silicon nitride, silicon dioxide, and poly-Si to determine the most suitable sacrificial layer for device fabrication. Excellent film quality was obtained on all substrates investigated as determined by x-ray diffraction, IR absorption, and mechanical testing. Diagnostic and resonant structures were subsequently fabricated on the poly-Si based sacrificial layer coated substrates and characterized. On chip strain gauge characterization and Raman spectroscopy were both used to empirically determine the residual stresses present in the device structures. Resonance measurements were completed in order to ascertain Young's modulus of the mechanical films. Release of completed MEMS structures is accomplished using both wet and dry (XeF2) etch processes with excellent success realized in both cases. The results of these experiments, and target applications for the fabricated devices will be summarized in the proposed presentation.

5:00pm **MM-WeA10 Micro- and Nanotube Fabrication using Deposited Porous Silicon*, W.J. Nam*, *S. Bae, A.K. Kalkan, S.J. Fonash,* The Pennsylvania State University

There is a great deal of interest in micro- and nano- scale tube and channel structures. Conventional polycrystalline silicon (poly Si) material has been commonly used in such structures as a sacrificial layer. However, the etch rate of conventional poly Si sacrificial layers decreases rapidly in the case of the small etch access windows needed in etching small dimension structures due to reactant and reaction product transport limitations. Porous Si produced by electrochemical etching can eliminate these problems to some degree due to the multiplicity of transport paths to the access window but its formation requires wet processing. We solve this problem by introducing a new material, porous Si deposited using a high density plasma. Our deposited porous Si, produced using low temperature electron cyclotron resonance (ECR) deposition, can be made polycrystalline or amorphous and has a porosity that is controllable (up to ~90% porosity) without the need for any post-deposition etching. Used as a sacrificial layer, the material exhibits a high etch rate (1.5µm/min) since its connected-void morphology provides excellent transport pathways for the reactants and reaction products even when etched through a small access/exit window. The fast etch rate of this deposited porous Si prevents thinning or damaging of the other structural materials. We report specifically on structures using 500 Å of silicon dioxide as the substrate coating and etch stop layer during the sacrificial (porous Si) layer removal. In these structures, silicon nitride was used for a capping layer. The sacrificial porous Si material was etched out by using 5% tetramethyl ammonium hydroxide (TMAH), at either 30°C or 75°C. All layers (etch stop, sacrificial porous Si, and nitride) were produced in the same ECR tool.

Manufacturing Science and Technology
Room 304 - Session MS-WeA
Process Integration (Cu/Low-k/300mm)

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

2:00pm **MS-WeA1 Integration Challenges for Copper Metallization with Low-k Dielectrics*, B.L. Chin,*** Applied Materials **INVITED**

The transition from Al metallization to Cu has been implemented during the past several years and successfully introduced into several device products. This has resulted in improvement in device chip speed due to the resistivity reduction. To further decrease the RC time delay and minimize cross talk between interconnect lines, the transition to low-k materials has been actively investigated but the implementation has not been as rapid or straightforward. The convergence of Cu metallization with low-k dielectric has been hampered by the difficulty in replacing the present SiO@sub2@ with a low-k material that meets all the film property requirements: mechanical, thermal and electrical compatibility. Key integration issues for the low-k material include dual damascene pattern definition, adhesion of the barrier/ seed and adequate planarization. A review of the various materials and technologies (PVD, CVD) to deposit the barrier/ seed will be presented along with the pre-clean methods to ensure low via resistance. A survey of the different barrier films and barrier testing will illustrate the need for evaluating not only out-diffusion of Cu into the dielectric but also the in-diffusion of other components from the dielectric (e.g. diffusion of F from FSG to Cu). The currently used Ta-based barriers will be compared with composite layered structures and new materials. The necessity for decreasing the seed layer thickness for electroplating fill has placed a greater demand on the step coverage and resultant interface properties. Recent advances in electroplating technology may resolve this issue and its impact on integration with low-k materials will be highlighted. These challenges will be further amplified with the introduction of porous low-k materials and may force the implementation of other technologies to satisfy the requirements for sub- 0.1 µm devices.

2:40pm **MS-WeA3 Adventure of the first 300mm Pilot Line*, M. Peschke,*** Semiconductor 300 GmbH&Co.KG, Germany **INVITED**

The transition in wafer size has always been a risky project in the past. Even for very sophisticated and wealthy companies it was a painful experience. Using the synergy of the know how and share the costs Infineon Technologies and Motorola announced in 1998 a Joint venture (Semiconductor 300) for a 300mm pilot line located in Dresden. Based on the standards provided by i300i and Selete (i.e. CIM/ Automation or FOUP requirements, process specifications), the equipment manufacturers could provide the simultaneous availability of all required tools. When SC300 started first test results were already available and the visibility "first sample of a working transistor" was already shown by Motorola. The factors to influence the productivity improvement of 30% per year, become smaller so the manufacturing effectiveness has to gain to keep the improvement rate. The focus was directed to reliability of the tools, whereas the process performance was assessed as a "must criteria". The equipment industry has grown tremendous in the last years so the financial strength and expertise has grown as well. All the new ideas of improvement which could not implemented in the existing tool set went into the design of the new generation. A key factor for the success of the SC300mm project has been the open relationship with the equipment suppliers. Jointly the tools were tested and stressed under manufacturing conditions. The technology which was used to ramp up the 300mm pilot line was a state of the art DRAM product. With the redundancy of a DRAM the impact of defect density is limited and so learning cycles were faster. With the help of the local infrastructure of the 200mm production line, which ran the same product, problems were solved faster. The success of the first 300mm pilot line nine month after tool installation, demonstrates the potential of the existing tool set.

3:20pm **MS-WeA5 Cluster Formation on Copper Evaporated Onto Dow Cyclotene 3022*, E. Sacher,*** *D.-Q. Yang, S. Poulin, S. Rodrigues, L. Martinu, M. Meunier,* Ecole Polytechnique, Canada

Dow Cyclotene 3022 is a low permittivity polymer used in the microelectronics industry. It is made through the Diels-Alder polymerization of bis-benzocyclobutene-terminated divinyl siloxane monomers. Key Cu integration issues concern the adhesion of patterned Cu lines and the stability of the Cu-polymer interface to metal diffusion. Photoacoustic FTIR and XPS have shown that the Cu atoms interact asymmetrically with the aromatic rings of the Cyclotene to give weak bonding across the interface. XPS, XRD, AFM, TEM, spectroscopic ellipsometry, and other techniques, have shown that the Cu exists in the form of surface clusters. TEM micrographs, for example, show that a nominal 3.2 nm deposit exists in the form of irregular clusters with an average diameter estimated at 9 nm. This may be compared with an XPS estimate, based on an intensity comparison at two different orbital energies, which suggests that the clusters are spherical and about 7 nm in size. The weak bonding permits surface diffusion, which causes cluster coalescence on annealing, although there is no evidence, from any technique available to us, of diffusion into the bulk Cyclotene. The structure and properties of the Cu/Cyclotene interface will be compared with adhesion studies by microscratch and adhesive tape peel tests.

3:40pm **MS-WeA6 FSG Film Characterization and Process Development for Copper/Damascene Technology*, J.S. Martin,*** *K.J. Taylor, J.D. Luttmer, A.R.K. Ralston, T.D. Bonifield, J.A. West,* Texas Instruments, Inc.*; C.T. Adams, K.-H. Chew, A. Bayman, B. van Schravendijk,* Novellus Systems, Inc.

The microelectronics industry is transitioning from wiring devices with aluminum and oxide-based interconnect structures to damascene-based integration, with both copper and low-k materials. Toward this end, we outline the process technology and material characterization for a fluorosilicate glass (FSG) developed specifically for copper/damascene technology, where both the via and metal line are embedded in FSG at six levels. We compare FSG deposited in both high density plasma (HDP) and standard PECVD reactors, for K values within the range 3.50 - 3.70. Fluorine loss and water absorption are appreciably less for HDP-FSG films. We note two additional issues for FSG processes and films. First, adhesion to subsequently deposited PECVD silicon nitride is problematic and delamination increases with thicker FSG films. Second, deposition temperature strongly influences in-film [F], but for systems without active wafer temperature control, wafer temperature, and hence in-film [F] depends on the substrate dopant concentration. We briefly outline our methods for actively controlling wafer temperature to ± 5°C during deposition and monitoring [F] in-line via X-ray fluorescence (XRF). HDP-FSG thin films are thus deposited with active temperature control, and in-film [F] is controlled to within ± 0.2 atomic percent, as measured by XRF. Most important, by systematically decreasing in-film [F] over a 25% range, we observe that K-value increases by 0.10 and adhesion to silicon nitride significantly improves. We view this as a viable FSG process, applicable at the 0.18 µm and 0.13 µm nodes.

4:00pm **MS-WeA7 300mm Manufacturing Meterology Needs*, R. Goodall,*** Sematech **INVITED**

PLEASE SEND US AN ABSTRACT. Thank you.

Processing at the Nanoscale/NANO 6
Room 302 - Session NS+NANO6-WeA

Nanoscale Modification of Materials

Moderator: R.E. Palmer, The University of Birmingham, U.K.

2:00pm **NS+NANO6-WeA1 Selective-Area Chemical Vapor Deposition Using AFM-Patterned Silicon Nitride Growth Mask*, S. Gwo,*** *S.-W. Lin, Y.-C. Chou, T.T. Chen,* National Tsing-Hua University, Taiwan*; T. Yasuda, S. Yamasaki,* Joint Research Center for Atom Technology (JRCAT), Japan*; T.-S. Chao,* National Nano Device Laboratory, Taiwan

Silicon nitride (Si@sub 3@N@sub 4@) is a very robust material against oxidation and etching and is typically used as an oxidation mask. Here we report atomic force microscope (AFM)-based local oxidation of Si@sub 3@N@sub 4@ and its applications in nanofabrication. Owing to very large etch and growth selectivities among Si@sub 3@N@sub 4@, SiO@sub 2@, and Si, AFM nanolithography using Si@sub 3@N@sub 4@-mask could be used to both "subtractive" (selective-area anisotropic etching of underlying substrate) and "additive" (selective-area chemical vapor deposition) fabrication processes of nanostructures through the openings on the Si@sub 3@N@sub 4@ resist mask. Using this AFM-patterning method combined with a novel design of bilayer growth mask, which is entirely compatible with the existing microelectronic processes, synthesis of ultrahigh packing density and ordered nanostructure becomes readily achievable.

2:20pm **NS+NANO6-WeA2 Fabrication of Nanoscale Templates by Chemical Lithography*, A. Gölzhäuser,*** *W. Geyer, V. Stadler, W. Eck, M. Grunze,* Universität Heidelberg, Germany*; T. Weimann, P. Hinze,* Physikalisch Technische Bundesanstalt, Germany*; K. Edinger,* University of Maryland

Nanostructure fabrication requires precise lithographic tools and smart materials that can be modified in a controlled manor. Recently, we discovered that self-assembled monolayers of biphenylthiols are crosslinked by electrons and can be utilized as negative resists.@footnote 1@ Crosslinked biphenyls can also be applied as stabilizing spacer groups during modifications via chemical lithography, specifically the conversion of NO@sub 2@ to NH@sub 2@ end groups.@footnote 2@ Based on these findings, we fabricated templates by high resolution electron beam lithography. We used a Leica LION LV 1 system at a beam energy of 2.5 keV and doses between 10 and 50 mC/cm@super 2@. We also applied a simple and versatile projection technique using FIB structured stencil masks and low energy (50eV) electrons. The templates were characterized by contact and lateral force AFM. The finest structures have lateral dimensions of ~20nm. We show that they can be used for a laterally controlled molecular deposition. @FootnoteText@ @footnote 1@ W. Geyer, V. Stadler, W. Eck, M. Zharnikov, A. Gölzhäuser, M. Grunze, Appl. Phys. Lett. 75, 2401 (1999). @footnote 2@ W. Eck, V. Stadler, W. Geyer, M. Zharnikov, A. Gölzhäuser, M. Grunze, Adv. Materials, in press.

2:40pm **NS+NANO6-WeA3 National Nanotechnology Initiative: Overview*, M. Roco***[1]*,* The National Science Foundation **INVITED**

PLEASE SEND US AN ABSTRACT. Thank you.

3:20pm **NS+NANO6-WeA5 Electronic Conductivity and Thermoelectric Measurements of Bismuth Nanoline Structures*, K. Miki,*** *A. Yamamoto, K. Sakamoto,* Electrotechnical Laboratory, Japan

Using the newly discovered characteristic structure of Bi perfect lines in Si(001) terraces, we have fabricated two new nanostructures of bismuth in silicon epitaxial layers and measured both their electronic and thermoelectric properties. Atomically perfect bismuth lines form in flat Si(001) surfaces around the temperature at which most of the bismuth desorbs from bismuth epitaxial layers. The lines are 1 nm wide and can be hundreds of nm long without kinks or other defects. In order to form multiple layers containing lines, segregation of the bismuth during subsequent silicon deposition was suppressed by further deposition of bismuth. In this way we fabricated three layers of Bi lines with undoped Si spacer layers 62 nm thick on an SOI (silicon on insulator) substrate, then capped it with 20 ML of silicon. We also fabricated a Bi delta doped structure: we intentionally destroyed most of the whole line structure by incompletely covering the surface with Bi and then heating the sample around 1100 degree C for 20 minutes. In this way we made five delta doped layers, separated by undoped Si spacer layers 20 nm thick. The layered structures were patterned into 1 micron x 100 micron bar-shaped devices through reactive ion etching, and metal contacts were made for transport measurements. By isolating the device on silicon oxide we eliminated electric leakage. The electronic measurements show that the delta doped structure is n type whereas the buried Bi line structure has metallic conductivity. We applied a temperature gradient to the buried Bi line structure along sample length of 100 micrometres, and observed a thermoelectric voltage linearly proportional to the temperature difference, of the order of 100 microvolts.

3:40pm **NS+NANO6-WeA6 Quantum-wire Arrays Fabricated by a High-pressure High-temperature Injection Process*, T.E. Huber,*** Howard University*; M.J. Graf,* Boston College*; C.A. Foss Jr.,* Georgetown University

Three-dimensional arrays of metals and semiconductor ultrafine wires can be synthesized by injecting its liquid melt into a porous anodic aluminium oxide (PAAO) template. This is a highly effective technique with a resolution that exceeds 10 nm in many cases. Nanowire arrays are attracting a great deal of attention because of their potential applications in electronics and optics and promise for studying quantum confinement effects. The semimetal Bi is unique because, due to its extremely small effective mass, its Fermi wavelength is long, 25 nm. Therefore, quantum confinement effects should be readily observed in nanowires whose diameter are below ca. 25 nm. Large area (2 mm x 2 mm) arrays of parallel wires of Bi with diameter as small as 20 nm, lengths of 30 - 50 mm, and packing density as high as 10@super 11@ cm@super -2@ have been fabricated. The nanowires are essentially single crystalline and oriented. We have found a resistivity enhancement and a very large positive magnetoresistance. For small diameter wires a resistance maximum is observed. The nanowires contact resistance and doping effects are discussed. The experimental results are discussed in terms of the semimetal-to-semiconductor transition, classical size effects and mesoscopic phenomena. Bulk Bi and Bi-Sb alloys are the best thermoelectric materials at 77 K; the nanowire array composites, especially the 1D Bi quantum wire systems, are expected to show improved properties.

4:00pm **NS+NANO6-WeA7 Transport Study of Single Bismuth Nanowire Fabricated by Silver and Silicon Nanowire Shadowmask*, S. Choi,*** *M. Leung, G. Stupian, N. Presser,* The Aerospace Corporation*; S. Chung, J. Heath, A. Khitun,* University of California, Los Angeles*; A. Balandin,* University of California, Riverside

We have carried out measurements of the electrical conductivity of a single bismuth nanowire fabricated by low energy electron beam lithography using silver/silicon nanowire shadowmasks. The nanowires examined have characteristic dimensions slightly below the critical diameter (about 50nm) at which a semimetal to semiconductor phase transition was predicted to occur. Our results reveal a semiconductor-like temperature dependence of the electrical conductivity of a bismuth nanowire which is strikingly different from the bulk dependence. We have also developed a theoretical model which adequately describes the dependence of the electrical conductivity and energy band gap on the diameter of bismuth nanowires and other parameters. The experimental data presented may be crucial for suggested thermoelectric application of bismuth nanowires.

4:20pm **NS+NANO6-WeA8 Conductance Anisotropy in a Mesoscopic Array of Atomic Wires: Ga/Si(112)@footnote 1@*, K.J. Yoo*,** *S. Tang,* University of Tennessee*; P.T. Sprunger,* Louisiana State University*; H.H. Weitering,* University of Tennessee

In recent years, researchers at the Naval Research Laboratory have used the Si(112) surface as a template for the fabrication of a mesoscopic array of single-atom-wide gallium wires or quantum wires.@footnote 2@ The structural uniformity of the wire array appears far superior to those created by nanolithographic methods. We have characterized this Ga/Si(112) hetero-structure with Scanning Tunneling Microscopy, Angle-Resolved Photoelectron Spectroscopy (ARPES), and Si 2p core-level spectroscopy. The electrical conductivity of the wire-array was measured as a function of temperature in ultrahigh vacuum using the four-point-probe technique parallel and perpendicular to the quantum wires. The parallel conductivity has a temperature-dependence characteristic of a semiconductor. In contrast, the conductivity perpendicular to the wires appears metallic. This unexpected result can be understood on the basis of first-principles calculations by Flores and coworkers in Madrid @footnote 3@, which indicate that the band effective mass in the perpendicular direction is close to the free electron mass (m*=1.3 m@sub e@) whereas the effective mass in the parallel direction is very large (m*> 5.5 m@sub e@). The main features of the theoretical surface-state band structure have been confirmed with ARPES. Contributions to the electrical

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[1] **Featured Speaker - Science and Technology in the 21st Century**

conductivity by the space charge layer beneath the surface have been calculated based on core level measurements of band bending. These contributions were subtracted to determine the electrical conductance solely through the quantum wires. @FootnoteText@ @footnote 1@Work supported by National Science Foundation(DMR-9705246). @footnote 2@A. A. Baski, S. C. Erwin, and L. J. Whitman, J. Vac. Sci., B14(2), 992(1996). @footnote 3@F. Flores, in private communication.

4:40pm **NS+NANO6-WeA9 Time Evolution of Ag Nanowires Grown on Ag/GaAs(110) Surfaces***, **H.-B. Yu**, C.-S. Jiang, X.-D. Wang, C.-K. Shih,* University of Texas at Austin

We have studied an unusual 'shrink-expand' behavior of Ag nanowires grown on Ag films using scanning tunneling microscope (STM). Ag films were prepared using low temperature deposition onto UHV in-situ cleaved GaAs(110) surfaces, followed by room temperature annealing. The film thus formed, below or around 6 ML, are atomically flat with voids distributed in the film. After the film becomes smooth, atoms inside the voids continue to transfer to the top Ag surface and form nanowires. Some of the nanowires have aspect ratios greater than 100:1. The nanowire length growth was monitored with STM, showing linear growth rate with time, while keeping the same width. After growing to certain length, the wires start to shrink, and at the same time, their widths expand by about 1.4 nm. After this shrinking process, the Ag wires continue to grow linearly in time before it takes on another 'shrink-expand' process. This 'shrink-expand' behavior can be observed on nanowires with no voids surrounded, but also on wires that are approaching the existing void edge, which indicating the repulsive interaction of nanowires with the edge of the voids. Detailed mechanism of this nanowire shape transition will be discussed.

5:00pm **NS+NANO6-WeA10 Ion Implanted Contacts to Nanostructures and Metallic Monolayers on Clean Surfaces***, **J.W. Nolan**, B.N. Cotier, M.J. Butcher, P.H. Beton, P. Moriarty, M.R.C. Hunt, A. Neumann,* University of Nottingham, UK*; V.R. Dhanak,* Daresbury Laboratory, UK*; A. Gundlach,* Edinburgh University, UK*; S. Thoms,* University of Glasgow, UK

Ion implanted (As) contact tracks with separations of order 200nm and depths ~20nm are formed in p-Si/SiO2 wafers. These tracks are investigated using scanning tunnelling microscopy (STM) in an ultra-high vacuum environment following removal of the SiO2 layer using a combination of wet etching and high temperature vacuum annealing in the range 600-1000oC. The ion implanted regions are activated by this anneal and are slightly depressed (by ~5nm) as compared with the surrounding surface but co-exist with the Si(100)-2x1 and Si(111)-7x7 surface. Core level photoemission studies of control samples which have been uniformly implanted show that As desorbs from the near surface region for temperatures >900oC, the temperature at which the oxide layer is thermally desorbed, but this leads to an insignificant change in resistance of the tracks. The ion implanted regions form high impedance reverse biased p/n junctions with a p-type substrate and adjacent implanted tracks may be shorted by the deposition of thin metallic films. The shorting resistance of these structures has been measured using an in-situ electrical prober and results are correlated with the morphology of the metallic layer. For samples annealed below 900oC the oxide layer is not desorbed and a shorting resistance ~20kOhms is observed for a Ag film of thickness 0.5nm. At higher annealing temperatures this shorting resistance is much higher due in part to As desorption and in part the island morphology of the Ag film. The process is compatible with H termination and de-passivation and we report results on metallic adsorption on depassivated wires ~1-5nm wide.

Organic Films and Devices
Room 313 - Session OF-WeA
Self-Assembled Monolayers: Electron Transfer and Film Properties

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

2:00pm **OF-WeA1 Rates of Interfacial Electron Transfer Across Well-Defined Model Interfaces***, **C.E.D. Chidsey**,* Stanford University **INVITED**

The injection of electrons and holes into molecular or polymeric organic materials is a key process in many organic devices such as light-emitting diodes, transistors and sensors. Injection is normally accomplished by the thermal transfer of electrons across interfaces between metallic or semiconducting electrodes and the organic material. I will discuss methods to measure the rate of this process across well-defined model interfaces and our developing understanding of the role of molecular structure in determining these rates.

2:40pm **OF-WeA3 Charge Transfer in Alkanethiol Self-Assembled Monolayers on Au Surfaces***, **K. Son**, H.I. Kim, J.E. Houston,* Sandia National Laboratories

Charge transfer in self-assembled monolayers (SAM) has been studied extensively for molecular electronics applications, and Scanning Probe Microscopy studies have led to a general agreement on the role of force induced structural deformation on the conductivity of alkyl based SAMs. However, controversies about the level of tip/sample contact remain unresolved, and the evidence for structural deformation is vague. Here we investigate charge transfer in alkanethiol SAMs on Au(111) using Interfacial Force Microscopy (IFM). This technique enables the first simultaneous measurements of conductivity, normal-force, and friction over the entire range of tip/sample interaction. For alkanethiols (C@sub n@H@sub 2n+1@SH, n>10), we observe no current until the IFM tip makes physical contact with the SAM surface (down to the fA level). The current then increases exponentially with applied stress. Current and force profiles track each other from the initial conduction point, and both show a strong correlation with the rise in friction. I-V data taken at various force levels show both linear and resonance regions while the slope and the transition point are strongly dependent on the force level as well as molecular chain length. Based on these results, we conclude that the current flow through SAM films occurs by a tunneling process with necessary tip/film contact. We attribute the conductivity increase to the force-induced changes in film structure resulting in a redistribution of the film's electronic states, as evidenced by both the friction and the I-V characteristics. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the U.S. Dept. of Energy under Contract DE-AC04-94AL85000.

3:00pm **OF-WeA4 Low Energy Electron Microscopy Studies of the Growth of Thin Pentacene Films***, **R.M. Tromp**, F. Meyer zu Heringdorf, C. Dimitrakopoulos, J. Shaw,* IBM T.J. Watson Research Center

We have used Low Energy Electron Microscopy (LEEM) to study the growth and structural evolution of thin pentacene films on a variety of surfaces and substrates. LEEM allows the growth process to be followed in real time with high spatial resolution (5 nm), and at videorate. Thin film nucleation and subsequent growth can be studied in much detail. For instance, diffusion of pentacene on the starting substrate (for instance clean Si, or SiO2) is isotropic, giving rise to fractal two-dimensional islands. These islands are nonetheless crystalline. The second layer grows on this crystalline template, with highly anisotropic diffusion. Substrate and substrate preparation give a certain degree of control over the polycrystalline grain size. In addition to the growth morphology, LEEM allows the observation of what appear to be molecular size defects in the film, giving rise to charge trapping. Such traps charge and discharge on timescales of 0.1 to several seconds. The density of such traps depends critically on the growth conditions. It appears that traps can be eliminated by careful control of the evaporation parameters. These studies, the first to observe the growth of organic semiconductors in real space, and in real time, enable a detailed understanding of the basic processes underlying the growth process. Direct parallels can be drawn between organic thin film growth, and the epitaxial growth of very different materials such as Si and Pt. These basic insight allow a careful optimization of the growth conditions, optimizing defect densities, grain size, and growth morphology.

3:20pm **OF-WeA5 Self-assembled Monolayers on Silicon Surfaces via Si-O Linkages***, V. Boiadjiev, **R.C. Major**, X.-Y. Zhu,* University of Minnesota

Monolayer assemblies on silicon surfaces are of interest for a number of technological reasons. Here, we present a novel, two-step strategy for assembly formation directly on silicon surfaces. In the first step, a H-terminated Si(100) or Si(111) surface reacts with Cl2 to give a Cl-capped surface. In the second step, the Cl-Si surface is immersed in an alcohol/isooctane solution for monolayer formation via Si-O linkages, with the removal of surface Cl likely in the form of HCl. This reaction mechanism is confirmed by X-ray photoelectron spectroscopy. X-ray reflectivity measurement shows that the thickness of the monolayer film is close to molecular dimension and the density is about 85% of that in crystalline paraffine. Fourier transform infrared spectroscopy and water contact angle measurements suggest that the alkyl chains within the monolayer possess, to a limited degree, conformational order. Atomic force microscopy image with molecular lattice resolution shows intermolecular distance corresponding to close packing of alkyl chains. The monolayer coatings show both chemical and mechanical stability. The possible mechanism for monolayer assembly formation on covalent Si surfaces is discussed.

3:40pm **OF-WeA6 Friction Force Microscopy Study on Photodegradation of Organosilane Self-assembled Monolayers Irradiated with a Vacuum Ultraviolet Light at 172 nm***, **H. Sugimura**, K. Hayashi, O. Takai,* Nagoya University, Japan

Photodegradation of organosilane self-assembled monolayers (SAMs), under the presence of atmospheric oxygen molecules, has been studied using an excimer lamp radiating vacuum ultra-violet (VUV) light of 172 nm in wavelength. A SAM was prepared on each of Si substrates covered with native oxide from a precursor of octadecyltrimethoxysilane by a chemical vapor deposition method.@footnote 1@ The SAM-covered samples were photoirradiated under a controlled pressure from 10 to 10@super 5@ Pa. As confirmed by water contact angle measurements, infrared reflection-absorption spectroscopy and X-ray photoelectron spectroscopy, the SAM was decomposed and removed due to the VUV-irradiation. This photodegradation mechanism is ascribed to dissociative excitation of C-C and C-H bondings in the organosilane molecules and to subsequently proceeded oxidation with atomic oxygen radicals generated simultaneously by the VUV-irradiation of O@sub 2@ molecules. Furthermore, micropatterning of the SAM was demonstrated by a simple photomask-contacting method.@footnote 2@ Due to a distinct difference in frictional force in contact-mode atomic force microscopy between the VUV-irradiated and unirradiated regions, the photoprinted pattern was clearly imaged. The VUV-irradiated region showed stronger frictional force than the unirradiated SAM surface. Patterning conditions were optimized based on these results obtained by frictional force microscopy. A micropattern of 2 µm in width was successfully photoprinted on the SAM. @FootnoteText@ @footnote 1@A. Hozumi et al. Langmuir,15 (1999) 7600. @footnote 2@H. Sugimura et al. Langmuir,16 (2000) 885.

4:00pm **OF-WeA7 Generation of Reactive Intermediates on Platinum by Photolysis of Pyridyl-@alpha@-Diazocarbonyl Self Assembled Monolayers***, **J.L. Pitters**, D.K. Adkinson, P.R. Norton, M.S. Workentin,* University of Western Ontario, Canada

There is considerable current interest in understanding the chemistry of organic molecules as Self Assembled Monolayers (SAMs) on metal surfaces. Much of the effort in this regard has focused on long chain alkyl thiols on gold with the ultimate goal of being able to control the interfacial properties for use in wide ranging material and device applications. However, there has been a growing interest in small molecule SAMs and their relevance to surface modification. We have prepared a series of photoreactive pyridine based molecules for study as SAMs on single crystal Pt. Monolayers (saturated layers) of pyridyl-diazoketones, pyridyl-diazoesters and pyridyl-diazoaldehydes have been characterized using Ultra High Vacuum (UHV) Reflection Absorption Infrared Spectroscopy (RAIRS) and other surface sensitive techniques. Diagnostic out-of-phase C=N=N and C=O absorptions indicate that the diazo and carbonyl groups are stable on the Pt surface and that binding most likely takes place through the pyridyl nitrogen as is the case in most substituted pyridines. Upon exposure to 300-400 nm light, the diazo group releases nitrogen quantitatively to yield either carbene or ketene intermediates depending on the original substrate. Most notably is the formation of a ketene functionality (C=C=O) at the interface through the Photo-Wolff rearrangement. The ketene is identified by the diagnostic out-of-phase infrared absorption at approximately 2110 wavenumbers. This study represents the first direct spectroscopic evidence of a photoreactive diazo-carbonyl monolayer and the subsequent photochemical formation of a stable ketene monolayer on a metal surface. Ketene and carbene reactivity is versatile and we believe that knowledge of the interfacial reactivity in the present systems can be extended to provide a novel surface for template synthesis and surface modification.

4:20pm **OF-WeA8 X-Ray Induced Changes in Thiol-SAMs on Gold***, B. Zeysing, T. Eickhoff,* University of Hamburg, Germany*; W. Drube,* Hamburger Synchrotronstrahlungslabor HASYLAB at Deutsches Elektronensynchrotron DESY, Germany*; **A. Terfort**,* University of Hamburg, Germany

Self-assembled monolayers (SAMs), in particular SAMs of alkanethiols on coinage metals, such as gold, receive a growing interest as convenient possibility to modify surfaces in an experimentally simple but very well adjustable manner. Since these layers are very thin (about 0.5 to 10 nm), they are typically characterized by surface sensitive techniques, often involving x-rays. On the other hand, it is known for some time that these monolayers are subject to massive changes upon irradiation, mainly caused by primary or secondary electrons generated in the supporting high-z material, which penetrate the monolayer.@footnote 1-4@ These electrons remove binding electrons from the molecules by impact ionization, leaving positive charges (holes) within the surface molecules. In alkane chains these holes remain localized and trigger chemical reactions. This results in altered monolayers with different properties and'mixed' results which are usually difficult to interpret. In our talk, we present results obtained by using synchrotron radiation based methods to demonstrate how fast monolayers transform under illumination with x-rays, and what the detailed mechanism of this transformation is. Using total external reflection x-ray photoelectron spectroscopy (TER-XPS),@footnote 5@ we could determine the fate of the sulfur atoms. By understanding the mechanisms of destruction, we were able to design SAMs with significantly increased stability towards x-rays. @FootnoteText@ @footnote 1@Wirde, M.; Gelius, U.; Dunbar, T.; Allara, D. L. Nuclear Instr. Methods Phys. Res. B 1997, 131, 245. @footnote 2@Zubragel, Ch.; Deuper, C.; Schneider, F.; M. Neumann, N.; Grunze, M.; Schertel, A.; W@um o@ll, Ch. Chem. Phys. Lett. 1995, 238, 308. @footnote 3@Olsen, C.; Rowntree, P. A. J. Chem. Phys. 1998, 108, 3750. @footnote 4@Zerulla, D.; Chass@aa e@, T. Langmuir 1999, 15, 5285. @footnote 5@M.J. Bedzyk, G.M. Bommarito, J.S. Schildkraut, Phys. Rev. Lett. 1989, 62, 1376.

4:40pm **OF-WeA9 Surface Stress of Self-Assembled Alkanethiols on Gold-Coated Cantilevers***, **M. Godin**,* McGill University, Canada*; P.J. Williams,* Acadia University, Canada*; V. Tabard-Cossa, P. Grütter,* McGill University, Canada

The commercial availability of atomic force microscope (AFM) microcantilevers has made possible the development of new ultrasensitive techniques aimed at measuring nanoscale quantities such as mass, heat and surface stress. We have adapted standard gold-coated silicon nitride AFM cantilevers as a chemical sensor. During chemical sensing, the cantilever bends due to the surface stress associated with the adsorption of specific target molecules onto a single side of the cantilever, which has been coated with a receptive layer. We have used our cantilever sensor to measure the surface stress associated with the self-assembly of alkanethiols on gold-coated cantilevers. This surface stress is strongly associated with the structural organization of the self-assembled thiol monolayer, as well as molecular chain-length. We will discuss the importance of the quality of the gold receptive surface with respect to thiol monolayer formation, as well as the kinetics of vapor-phase self-assembly of alkanethiols onto gold.

5:00pm **OF-WeA10 Self-assembled Monolayers of 6-Phenyl-n-Hexanethiol and 6-(p-Vinylphenyl)-n-Hexanethiol on Au: An Investigation of Structure, Stability and Reactivity***, **L. Duan**, S. Garrett,* Michigan State University

The structure, stability and reactivity of 6-Phenyl-n-Hexanethiol (PHT) and 6-(p-Vinylphenyl)-n-Hexanethiol (VHT) monolayers on Au (111) is presented. RAIR spectroscopy, ellipsometry and STM have been used to characterize the self-assembled monolayers (SAMs). The RAIR spectral data indicated that both molecules chemisorbed on gold as thiolates, however, the alkyl chains were disordered for both SAMs. We investigated the structural changes of PHT monolayers with decreasing molecular surface density by annealing in ultrahigh vacuum. Three different "stripe" phases have been observed by STM. All three condensed phases are characterized by alignment of the molecular axes with the surface plane, but with decreasing degrees of out-of-plane interdigitation. On the contrary, VHT molecules are oriented almost parallel to the surface normal at room temperature. Polymerization of VHT SAMs can be achieved by either UV-light irradiation or annealing. The polymerization process was followed by RAIR spectroscopy by observing the decrease in peak intensities associated with vinyl functionalities. UV-light irradiation produced long chain polymers with ~70% conversion rate after 25 min, while annealing produced short-chain polymers with CH@sub 3@ as the end group. The UV-light polymerized film is more robust to heating than thermally polymerized film.

Plasma Science and Technology
Room 310 - Session PS1+MS-WeA
Sensors and Control in Plasma Processing

Moderator: I.P. Herman, Columbia University

2:00pm **PS1+MS-WeA1 Supervision of Plasma Processes using Multiway Principal Component Analysis*, D. Knobloch,*** *F.H. Bell,* Infineon Technologies AG, Germany*; K. Voigtlaender, J. Zimpel,* Fraunhofer Institute IVI, Germany

In modern IC-manufacturing lines, plasma processing is still one of the most complex single process steps. The trend towards even smaller feature sizes and greater wafer diameters results in the need of better process and equipment control. In previous studies@footnote 1,2@, we have shown that an OES-system, based on a multiband CCD-spectrometer and operated with a home built software, can be used for run-to-run and real time process control. In this work, we show how we extended our software tool in order to improve data analysis. A MPCA (Multiway Principal Component Analysis) has been implemented that allows extraction of key numbers from spectral data simultaneously in time and wavelength. Key numbers are extracted for single processes as well as for run-to-run variations. As an example, the chamber conditions as a function of rf-hours and process mix is characterized by MPCA key numbers. It is shown, that the key numbers represent the cleanliness of the plasma chamber that depends on the process mix. Consequently, the key numbers can be used to establish an optimum product flow in the chamber in order to optimize wet clean cycles and control particle generation. Furthermore, we demonstrate, how fault detection, such as determination of gas flow variations or chamber leaks, can be achieved. The MPCA key numbers of misprocessed wafers show variations to processing of good wafers and can be correlated to certain equipment or process faults. However, the establishment of a catalogue with spectral pattern of fault classifications, such as chamber leaks, is needed. Consequently, preventive maintenance is triggered in order to fix the observed equipment faults as soon as possible. @FootnoteText@ @footnote 1@ D. Knobloch et al, November 1998, AVS 45th International Symposium, Baltimore @footnote 2@ D. Knobloch et al, October 1999, AVS 46th International Symposium, Seattle

2:20pm **PS1+MS-WeA2 Sensors and Control in Plasma Processing*, J.C. Arnold*,** *M.J. Hartig, C.F. Pfeiffer, J.A. Rivers, M.L. Johnson,* Motorola Semiconductor Products Sector **INVITED**

Even with the entrance of such processes as CMP and electrochemical deposition into the mainstream of semiconductor manufacturing, plasma processes remain among the most complex processes in the fab as well as among the most difficult to sustain. Furthermore, plasma deposition, etching, and cleaning processes are so numerous in typical product flows that the potential economic impact of plasma tool or process breakdowns is tremendous. The impetus for application of advanced sensors and automatic controls to these processes has been clear for years; however, widespread deployment of these devices and techniques in high volume manufacturing has been elusive. In this presentation, we will examine reasons for the apparent weakness in the pace at which sensors and controls have been adopted. We will begin with consideration of the terms "sensor" and "control" as related to the current state of the art in plasma processing. We will evaluate some of the sensor and control industry's current offerings in the context of the sensor and factory CIM system's ability to provide the "Acquisition - Analysis - Action" chain of three characteristics which we believe to be essential for adding value in the manufacturing environment. Finally, we will offer some end user perspectives on how changes in the business relationships between sensor and software vendors, capital equipment suppliers, and device manufacturers would facilitate more rapid and effective transfer of new techniques from the research lab to the production floor.

3:00pm **PS1+MS-WeA4 Run-to-Run and Real Time Process Control of Plasma Processes using an Inductive Antenna with Microsecond Resolution*, J. Mathuni*,** *F.H. Bell, D. Knobloch,* Infineon Technologies AG, Germany

Equipment and process stability during the fabrication process of integrated circuits is one of the main issues in current and future production lines. This is particularly mandatory for plasma processes. Intelligent run-to-run and real time control using plasma sensors help to prevent wafer scratches or misprocessing and to monitor chamber drifts, e.g. caused by damaged reactor walls or polymer coating on chamber walls during wet cleans. We have implemented the real time control of plasma processes using an in house developed antenna that measures the electric field of the plasma with microsecond resolution. Introduction of this sensor in our fabrication lines was challenged by two factors, namely, the development of robust and low cost hardware and easy to use software including process and equipment related control algorithm. The latter needs special attention, since the time resolution in the range of microseconds results in a very high amount of data making intelligent data reduction techniques mandatory. The measurement technique requires a dielectric material between plasma and sensor that can be easily realized using the quartz endpoint window of the plasma chamber. The benefit of this sensor is demonstrated for applications such as arcing detection, a phenomenon that may occur during microseconds and results in yield killing particle generation, and process parameter dependencies, such as B-field and power analysis. As a result, preventive maintenance is automatically triggered by sensor data. Since the sensor allows electric field measurements with nanosecond resolution, analysis of pulsed plasmas could be a further application.

3:20pm **PS1+MS-WeA5 Improved Utility of Microwave Energy for Semiconductor Plasma Processing through RF System Stability Analysis and Enhancement*, P.W. Rummel*,** *T. Grotjohn,* Michigan State University, US

The bulk of today's semiconductor plasma processing equipment utilizes RF energies at frequencies from 50 KHz to 60 MHz for deposition, etching, cleaning and various other processes. One of the impediments to utilizing microwave energy for these processes is the inherent instability often encountered with systems operating at frequencies of .5 to 2.45 GHz. Systems with plasma loads excited by resonant antennas, impedance matched by resonant circuits or cavities, and powered by generators of various source impedances are invariably unstable over some operating conditions. For microwave systems, this instability typically manifests itself as a propensity for the plasma to extinguish or rapidly change to a lower density as the impedance matching device is adjusted to minimize reflected power to the microwave generator. This paper shows why this instability exists and how a microwave driven plasma system can be modified to achieve better stabilization. A Matlab Simulink model and a state-model control analysis are used to identify system parameters that affect system stability and to predict the results of modifying those parameters towards the goal of improving stability. A plasma system utilizing a microwave cavity plasma reactor operating at 2.45 GHz. is first characterized to develop the models, and then modified to improve stability and illustrate the models' predictions. A high correlation between predicted and measured system stability validates the method of using a control analysis to model plasma system stability.

3:40pm **PS1+MS-WeA6 Modeling and Real-time Control of RF Diode Sputtering for GMR Thin Film Deposition*, S. Ghosal*,** *R.L. Kosut, J.L. Ebert, L. Porter,* SC Solutions, Inc.*; D.J. Brownell,* Nonvolatile Electronics, Inc.*; H.N.G. Wadley,* University of Virginia, usa

This presentation describes the development and implementation of real-time control of rf diode sputter deposition resulting in significantly reduced wafer-to-wafer variation in device properties. Giant magnetoresistive (GMR) materials have very important applications which include technologies such as hard disk read-heads, computer memory, and sensors. One common configuration for thin-film sensors made by NVE is the GMR multi-layer consisting of sixteen metallic layers with individual layer thickness ranging from 15 to 40 @Ao@. For maximum GMR, the acceptable variation in layer thickness from one deposition cycle to another is very small (0.5 @Ao@ for the critical CuAgAu conducting layer). Before this work, there was considerable variation in GMR properties from wafer to wafer, despite no change in the nominal values of layer thickness. Sensitivity studies using a steady-state physical model (integrating plasma, sputter and atom transport processes) showed deposition thickness falling out of acceptable range with relatively small changes in rf power, chamber temperature, pressure, and electrode spacing. Careful experiments showed that while three of the four variables were controlled relatively well, there was significant variation (>1%) in total rf power delivered due to transients at the onset of the plasma. A controller was designed to compensate for transient fluctuations by turning off the plasma based on the time-integrated DC bias voltage at the target. This approach keeps the total rf energy input into the plasma constant for individual layers deposited. As a result of implementing this controller, the standard deviation (wafer-to-wafer) in average GMR % and in sheet resistance were both reduced by more than half. Additionally, guided by the integrated physical model, within-wafer uniformity was considerably improved by optimal electrode spacing and target shaping.

4:00pm **PS1+MS-WeA7 Productivity Solutions for Eliminating Within-Wafer and Wafer-to-Wafer Variability in a Silicon Etch Process through Plasma and Surface Diagnostics***, **E.A. Edelberg**, L.B. Braly, V. Vahedi, J. Daugherty,* Lam Research Corporation*; S.J. Ullal, A.R. Godfrey, E.S. Aydil,* University of California, Santa Barbara*; H.K. Chiu, H.J. Tao,* Taiwan Semiconductor Manufacturing Corp.

Various plasma and surface diagnostics were used to understand the root causes that lead to within-wafer and wafer-to-wafer variability in critical dimension (CD) loss in Si etch applications. It is found that the conditions of the reactor walls can play a significant role in determining the plasma properties and therefore the figures of merit of the etching process. Etch products from the wafer can adsorb and build up on the walls of the chamber leading to changes in the wall properties. These changes can lead to drifts in the plasma properties and cause wafer-to-wafer variability of the etch process. It is demonstrated that such drifts can be avoided by cleaning the walls of the reactor using Fluorine-containing plasmas in between wafers. We demonstrate that a fundamental understanding of the chemistry and composition of the deposited materials on the walls of the chamber and their relation to the gas phase species can be used to develop and optimize appropriate reactor wall cleaning processes. A multiple pass downstream Fourier transform infrared (FTIR) spectrometer is used to quantitatively measure the concentration of gas phase species such as SiCl@sub 4@ and SiF@sub 4@ in the reactor exhaust. In addition, a novel diagnostic technique based on the principles of multiple total internal reflection FTIR spectroscopy is used to measure, in situ, the presence and composition of material deposited or removed from the walls of the chamber. In particular, during Si etching processes with Cl@sub 2@/O@sub 2@ plasmas, the deposited films were found to be the byproducts of the etching reactions and contain Si, O and Cl. We show that performing a short plasma chamber clean with the appropriate chemistry between each wafer can reduce the wafer-to-wafer variability of both etch rate and CD bias. By performing an in situ clean after every wafer during a 0.13 micron gate etching process the wafer-to-wafer repeatability is reduced to 2nm (at 3 sigma).

4:20pm **PS1+MS-WeA8 Source Optimization for Magnetron Sputter-Deposition of NbTiN Tuning Elements for SIS THz Detectors***, **N.N. Iosad**,* Delft University of Technology, The Netherlands*; B.D. Jackson, J.R. Gao,* Space Research Organization of the Netherlands*; S.N. Polyakov,* Moscow State University*; P.N. Dmitriev,* Russian Academy of Sciences*; T.M. Klapwijk,* Delft University of Technology, The Netherlands

NbTiN is one of the most promising materials for use in the tuning circuits of Nb-based superconductor-isolator-superconductor (SIS) mixers for operating frequencies above the gap frequency of Nb (about 700 GHz). Device development requires stable and reproducible film properties. In this manuscript we compare the properties of NbTiN and NbN films obtained with a DC magnetron sputtering source using balanced and unbalanced magnetic trap configurations. This experiment shows that reducing the effectiveness of the magnetic trap by changing the magnet configuration is equivalent to reducing the sputtering pressure from the prospective of the film properties. We find that the properties of the films are not stable throughout the target life-time. Sputtering source with balanced configuration shows degradation of the NbN film properties as the target gets grooved for the fixed applied power and sputtering pressure. In contrast unbalanced sputtering source shows opposite behavior for the NbTiN films. We also show that it is possible to optimize the configuration of the magnetron magnets to produce stable and reproducible NbTiN films under the same gas pressure and applied power throughout the target lifetime.

4:40pm **PS1+MS-WeA9 Multiwavelength In-Situ Ellipsometry for Optical Coatings Fabrication: Optimal Control Strategies and Results***, **A. Hofrichter**, D. Kouznetsov, P. Bulkin, B. Drevillon,* Ecole Polytechnique, France

There is an increasing interest in adopting ellipsometric control for the manufacturing of optical filters. Ellipsometry does not relay on the amplitude of reflected signal, has very high sensitivity to both, thickness and complex refractive index, and can be used directly to probe growing surface, thus it is neither limited to transparent films nor depends on stability of light source. In comparison with such traditional techniques, as quartz crystal monitor and transmission/reflection spectrometer or laser interferometer, it is free of most their problems. However, interpretation of ellipsometric data is much more complicated and usually prevents application of ellipsometers for real-time process control in industrial environment. We present a robust algorithm for feed-back control of the PECVD deposition, based comparison of pre-computed ellipsometric trajectories with real-time data stream. Such approach allows to stop growth of each layer with high accuracy without performing complicated real-time inversion of ellipsometric data. Using our Integrated Distributed Electron Cyclotron Resonance (IDECR) PECVD reactor we performed depositions of multilayer and gradient optical coatings with good agreement with design. The next step will be inclusion of dinamic corrections of gas flows based on real-time determination of refractive index profile.

5:00pm **PS1+MS-WeA10 Low Open Area Endpoint Detection of Plasma Etching Processes - Limitations and Signal to Noise Characterization***, **B.E. Goodlin**, D.S. Boning, H.H. Sawin,* MIT*; M. Yang,* Texas Instruments, Inc.

In low open area contact and via etches, endpoint detection has proven very challenging in manufacturing, despite apparent successes in research and development. In our current studies, we are looking into critical issues preventing successful implementation of endpoint detection in a manufacturing environment. In particular, we have characterized two major limitations to endpoint detection inherent in many oxide etching processes. 1) Wafer Edge Limitations - Depending on processing conditions, the wafer edge contributes between 1% to 6% open area to the etch, and thus cannot be neglected in the endpoint detection scheme for etches where the patterned area is <10% open area. 2) Interferometry Limitations - When using optical emission spectroscopy, reflections from the wafer surface and the top electrode can lead to a significant source of noise that is very difficult to remove and can easily lead to false identification of endpoint. In addition to looking at limitations inherent in typical processes, we have also quantitatively compared performance of various sensors that have been proposed for endpoint detection. S/N was characterized for 4 different levels of open area (100%, 20%, 0.7%, 0.14%) for optical emission spectroscopy (OES), residual gas analysis (RGA), and RF Impedance sensors. Our findings indicated that the RGA had the best S/N capability at 0.14% open area, but the simple monochromator OES system was a close second, with good capability at 0.7%. Lastly, we have compared performance of multivariate OES systems with single wavelength monochromator systems and found that the monochromator showed greater capability for low open area endpoint detection. After revisiting some of the multivariate algorithms, it was discovered that the S/N improvements previously claimed for multivariate algorithms have been overstated. In some cases multivariate algorithms can actually decrease S/N.

Plasma Science and Technology
Room 311 - Session PS2-WeA
Feature Evolution

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

2:00pm **PS2-WeA1 Undercut and Bowing Characterisation in High Aspect Ratio Trenches of Poly-Si Etched in an ICP Reactor using Cryogenic SF6/O2 Chemistry Process***, **M. Boufnichel**,* University of Orleans, CNRS, France*; S. Aachboun,* ST Microelectronics, France*; G. Marcos, P. Ranson,* GREMI, France

In the last few years, deep trenches in silicon obtained by plasma etching have been widely studied for MEMS and/or microelectronics applications. A cryogenic method with an SF6/O2 chemistry plasma in an Alcatel ICP reactor is used to achieve deep trenches with high aspect ratio (>10) and high anisotropy. The etching rate in 2 µm wide and 100 µm deep trenches is about 3.5µm/min. The slope of the trenches can be adjusted from 88° to 90° and selectivity is higher than 300. However, profiles need to be improved, mainly by reducing the undercut and the bowing effects. Undercut is a lateral etching occurring under the mask which enlarges the trench opening and bowing is a local lateral etching located on the sidewalls and resulting in profiles destruction. This study deals with improvements in these effects. We investigated the outcome of process parameters (pressure, bias voltage, temperature, oxygen flow rate) and mask characteristics (nature, thickness, side slope, trench width and length). We tested several more or less conducting masks: oxide, thermal oxide created from TEOS gas, PSG (Poly-Silicate Glass containing 4% of phosphor), Sandwich (one layer of Si between two layers of SiO2) and Al. The different mechanisms responsible for undercut and bowing are finally discussed and evaluated.

2:20pm **PS2-WeA2 Origin of Sidewall Deposition during Cl@sub 2@/O@sub 2@ Etching of Sub Micron Features in Inductively Coupled Plasma Reactors***, **S.J. Ullal**, A.R. Godfrey, E.S. Aydil,* University of California, Santa Barbara*; E.A. Edelberg, L.B. Braly, V. Vahedi, J. Daugherty,* Lam Research Corporation

Shallow trench isolation (STI), a manufacturing technique used to isolate transistors in integrated circuits (IC), involves etching a trench of specific dimensions and shape into a silicon substrate in a high density inductively coupled plasma reactor. The trench is later filled with a dielectric and polished, resulting in a filled isolated shallow trench. To attain the best device characteristics, the filled trench must not contain any voids, which could be formed during filling, and avoided by engineering tapered sidewalls. These profiles are formed by redeposition of etch products on the sidewalls of the trench. The taper angle depends on a delicate balance between etching and redeposition on the sidewalls. In order to meet the stringent requirements of the IC fabrication industry, the taper angle on the sidewalls must be invariant to the position of the trench on the wafer and also be reproducible from wafer-to-wafer. To achieve these goals, a fundamental understanding of the nature and the origin of sidewall deposition is required. A typical STI etching process using Cl@sub 2@/O@sub 2@ gases was used to illustrate the dependence of sidewall deposition on chamber wall condition. A novel diagnostic method based on in situ multiple total internal reflection Fourier transform infrared spectroscopy was used to study the nature of the species deposited on the walls of the chamber. Etch products such as SiCl@sub x@ were detected by optical emission spectroscopy and Fourier transform infrared spectroscopy within, and downstream of the chamber respectively. Scanning electron micrographs of sub 0.25 µm features were examined to determine the profiles after etching. Simultaneous monitoring of the etch products in the gas phase, on the reactor walls, and in the reactor exhaust provides evidence which suggests that the deposition on the sidewall occurs due to a direct flux of etch products leaving the trench, rather than redeposition from the gas phase.

2:40pm **PS2-WeA3 Profile Simulation of Poly-Silicon Gate Features Etched with Cl2/HBr/O2 Plasmas***, **L.B. Braly**, D. Cooperberg, V. Vahedi,* Lam Research Corp.

The stringent requirements for line-width control during etching of sub 0.18-micron features for polysilicon gate applications demand a better fundamental understanding of the basic mechanisms that lead to line-width variation. Several groups have proposed various mechanisms for sidewall deposition on etched profiles, as well as mechanisms for etching Si with Cl2/HBr/O2. We are using our feature profile simulator (along with diagnostics) to test various mechanisms. Measurements of ion flux and polysilicon etch rates under various conditions are used to determine polysilicon etch yields for Cl2 and HBr. The sidewall deposition model includes direct (line of site) and redepostion of etch products on the feature sidewalls. The validity of these mechanisms is tested by comparing predicted etched features against real etched features. The simulator is also calibrated using data from profile wafers and over-hang wafers. We will show comparisons between predicted profiles and etched profiles under conditions where line-width growth (CD gain) and line-width loss (CD loss) are observed.

3:00pm **PS2-WeA4 Feature Profile Evolution during Pulsed Plasma Etching: Effects of Redeposition of Time-Dependent Etch Products***, **K. Ono**, H. Kousaka,* Kyoto University, Japan

Pulsed plasma etching has recently been attracting much attention as an advanced processing technique in the fabrication of microelectronic devices. The inclusion of pulse repetition frequency and duty cycle provides us with additional control variables to optimize the plasma process. In contrast to a relatively deep understanding of gas-phase chemical aspects of pulsed discharges and their effects on the processing, little work has been concerned with time-varying surface chemistry therein. This paper is concerned with the surface chemistry and the resulting profile evolution during pulsed plasma etching of Si in Cl@sub 2@. The time-dependent behavior of surface chlorination and ion-enhanced desorption of neutral Cl atoms adsorbed as well as reaction products SiCl@sub x@ from the surface is calculated in pulsed operation, using a simple model based on Langmuir adsorption kinetics. The etched profile evolution is then simulated for infinitely long trenches with different widths, taking into account the transport of ions and neutrals in microstructural features: geometrical shadowing of the structure, reemission of neutrals at the surface on incidence, and also redeposition of etch products from the surface being etched. The product species desorbed is assumed to be time-dependent, owing to reaction layer dynamics of the ion-assisted processes on a time-scale of micro to milliseconds: on a 1 ms time scale or shorter, tightly bound intermediates such as SiCl and SiCl@sub 2@ are released by momentum of the impinging ions, having large sticking probabilities on surfaces; on a time scale of tens of milliseconds and longer, the ion-enhanced formation of SiCl@sub 3@ and SiCl@sub 4@ is expected, having smaller sticking probabilities. The numerical results indicate that the effect of redeposition of etch products is more significant for pulsed discharges with shorter periods and smaller duty ratios, giving outwardly tapered profiles which are more pronounced on narrower pattern-width or higher aspect-ratio features. These results will also be compared with experiments.

3:20pm **PS2-WeA5 A Model for Si Etching in an Inductively Coupled SF@sub 6@/C@sub 4@F@sub 8@ Discharge***, **S. Rauf**, W. Dauksher, V. Arunachalam, P. Ventzek,* Motorola Inc.*; L. Lea, S. Hall,* Surface Technology Systems, UK

Fluorine rich plasmas such as SF@sub 6@ are known to rapidly etch Si. However, due to inadequate polymerization in SF@sub 6@, it becomes difficult to anisotropically etch high aspect ratio features with straight sidewalls. Polymerizing gases such as C@sub 4@F@sub 8@ are therefore added, either directly in the SF@sub 6@ discharge or in a separate polymerization step, to obtain the desired etch profiles. To understand the dynamics of Si etching in SF@sub 6@/C@sub 4@F@sub 8@, an integrated equipment and feature scale model has been developed for these plasmas. The model is based on the Hybrid Plasma Equipment Model (HPEM) and Monte Carlo Feature Profile Model (MCFPM) from the University of Illinois. The gas phase chemical mechanisms for SF@sub 6@ and C@sub 4@F@sub 8@ are primarily based on electron impact cross-sections available in the literature. Judicious adjustments have however been made to match model predictions with experiments. The surface mechanism for SF@sub 6@ assumes reactive ion etching due to the combined effect of F and energetic ions. The C@sub 4@F@sub 8@ discharge can etch (due to the synergistic effect of ions, CF@sub x@ radicals and F) and deposit polymer (due to CF@sub x@ radicals). The equipment model has been validated using gas phase measurements while the feature scale model has been calibrated using etch/deposition rate measurements and comparing model predictions to etch profiles. Results show that the SF@sub 6@ plasma is quite electronegative with SF@sub 6@@super -@ and F@super -@ being the dominant negative ions. CF@sub 2@ is the primary CF@sub x@ radical in the C@sub 4@F@sub 8@ discharge, and it is the main precursor to polymer formation. The paper investigates Si etching in both a multi-step process (with separate etching and passivation steps) and a combined SF@sub 6@/C@sub 4@F@sub 8@ discharge.

3:40pm **PS2-WeA6 An Integrated Model for Oxide Etch using Fluorocarbon Plasmas***, **V. Arunachalam**, S. Rauf, P. Ventzek, T. Sparks,* Motorola Inc.

Precise control of feature profile evolution during oxide etch using fluorocarbon plasmas is crucial to successful multilevel metallization. An important step in achieving this control is an understanding of the underlying physics and chemistry of the process across the various length scales ranging from the equipment scale to the feature scale, and their relationship to the equipment level knobs. This important step is captured through an integrated model comprised of an equipment scale model, a sheath model and a feature scale model. Using this model, the effect of typical process parameters on feature profile is examined in a generic inductively coupled plasma etching system. A surface chemistry mechanism developed using experimentally observed results is incorporated in the model. It includes processes such as polymer formation, ion assisted and thermal etching, ion sputtering and reflection, desorption and redeposition. The simulation results show the increase in anisotropy of the etch profile, decrease in the selectivity to the underlying silicon layer, and the transition from deposition to etch with increasing ion energy.

4:00pm **PS2-WeA7 Modeling of Trench Filling During Ionized Metal Physical Vapor Deposition@footnote 1@***, **J. Lu**, M.J. Kushner,* University of Illinois at Urbana-Champaign

Ionized Metal Physical Vapor Deposition (IMPVD) is used to deposit metal seed layers into high aspect ratio trenches in semiconductor processing. Conformal deposition and filling of trenches require an optimized ratio of neutral to ion flux, and optimized energy and angular distributions of the precursors. In this paper, we report on a reactor scale to feature scale computational investigation of Cu IMPVD in which this optimization is discussed. The computational tools used are the 2-dimensional Hybrid Plasma Equipment Model (HPEM) and the Monte Carlo Feature Scale Model (MCFPM). The HPEM produces species densities and source functions in the bulk plasma, and the trajectories of ions and neutral species onto the substrate. The MCFPM uses these fluxes and trajectories to evolve a deposition profile while considering energy and angular dependent deposition and sputtering probabilities. A surface diffusion algorithm was developed to avoid artificial dendritic growth. Cu deposition will be discussed for an inductively coupled plasma using a dc magnetron target. Typical operating conditions are 10's mTorr Ar buffer gas, 100's to 1000's kW ICP and magnetron power, and 10's V substrate bias. For constant ICP power, conformality improved and the likelihood of keyholes decreased as magnetron power decreased due to an increase in the ion-to-neutral ratio in the reactant fluxes. Micro-voids are sometimes produced for these otherwise "good" conditions due to microtrenching which occurs by ion-reflection neutrals during resputtering of the deposited metal. Similar effects are seen by increasing buffer gas pressure to increase ionization fraction. The consequences of surface diffusion on the profile will also be examined. @FootnoteText@ @footnote 1@Work supported by TAZ, Novellus, AMAT, SRC and NSF.

4:20pm **PS2-WeA8 Process Characterization for Tapered Contact Etch***, F.G. Celii, Q. He, J. DeBord,* Texas Instruments, Inc.*; **H. Sakima,*** Tokyo Electron America

The demands placed on lithography by the constant reduction in feature size can sometimes be alleviated in conjunction with the etch process. For line patterning, photoresist trimming gives a large etch bias and reduces linewidths well-below the lithography limit. For hole patterning, a tapered etch profile results in a bottom hole diameter which can be significantly smaller than the patterned CD. We report the characterization of contact etch processes which give variable sidewall taper angles. Patterning at 248 nm gave contact holes at ~0.19 µm diameter in photoresist over organic BARC. The contact stack (BARC/oxide/SiN, 6 - 10 kÅ total stack thickness) was etched in a medium-density TEL Dipole Ring Magnetron (DRM) system. Bottom hole diameters ranging from 0.17 µm down to 0.10 µm could be obtained by varying the oxide etch process, which included C@sub 4@F@sub 8@ or C@sub 5@F@sub 8@, O@sub 2@ and Ar. Moderate etch selectivity to SiN (>10:1) was needed because of the bi-level contact height (over gate or over active). Etched patterned wafers were characterized using top-down CD-SEM, cross-section SEM and TEM. Ex situ surface analysis of etched blanket wafers was made to test the model of fluorocarbon film control of etch selectivity. Electrical properties of the W-filled contacts will also be summarized.

4:40pm **PS2-WeA9 Understanding the Evolution of Trench Profiles in the Via-First Dual Damascene Integration Scheme***, **T. Kropewnicki**, K. Doan, B. Tang, C. Björkman,* Applied Materials

Many surprising shapes of via profiles and trench bottoms have been observed during trench etch of the via-first dual damascene integration scheme. The most common features are faceting of the existing via holes as the trench etch progresses and fencing around the via holes. These particular features can lead to problems during copper metallization and ultimately to device failure. Therefore, it is imperative that the evolution of these features be understood so that they can be avoided. This paper will present experimental results indicating that the evolution of these features is heavily dependent upon the existing via profile and whether bottom antireflection coating (BARC) or photoresist (PR) is in the via hole prior to starting the trench etch. The proposed mechanism for faceting of the via hole is preferential sputtering of the top edge of the via. Fencing results when BARC or PR on the via sidewall vertically mask the underlying oxide when the via wall is sloped. Our empirical model for fence and facet formation was confirmed by a simple profile simulator. Finally, several options for avoiding the evolution of fencing and faceting during the trench etch will be proposed.

5:00pm **PS2-WeA10 Microtrenching, Etching and Sidewall Passivation in Contact Holes and Edge Regions***, **B. Abraham-Shrauner**, C. Liu,* Washington University

Our analytical/numerical models for etching in semiconductor fabrication of integrated circuits are extended to include sidewall passivation and microtreching for contact holes (vias) and edge regions. The models fit oxide etch profiles in SEMS in a CF4/CHF3/Ar plasma.@footnote 1@ Neither grazing scattering of ions from the feature sidewalls@footnote 2@ nor the deviation of the ion trajectories by sidewall charging@footnote 3@ are needed to model mild microtrenching. The model for contact holes includes a new approximate analytic expression for the ion energy flux, Langmuir kinetics for the ions and etching neutrals and the flux for deposition neutrals. The deposition neutrals are modeled by an interpolation between shadowed and isotropic neutrals. The edge region (half trench) model may include enhanced microtreching by scattered ions or distortion of ion trajectories by sidewall charging. The basic shape of the etch profile of the half trench is determined by the ion energy flux and the deposition flux and most of the sidewall is a characteristic of the evolution PDE. @FootnoteText@ @footnote 1@ Etch profile data was furnished by M. J. Buie and J. T. P. Pender of Applied Materials. @footnote 2@ M. Schaepkens and G. S. Oehrlein, Applied Phys. Lett. 72, 1293(1998). @footnote 3@ T. J. Dalton, J. C. Arnold, H. H. Sawin, S. Swan, D. Corliss, J. Electrochem. Soc. 140, 2395 (1993).

Semiconductors

Room 306 - Session SC+EL+SS-WeA

Semiconductor Alloys

Moderator: P. Desjardins, Ecole Polytechnique de Montreal

2:00pm **SC+EL+SS-WeA1 Si-Ge Heterostructures***, **K.L. Wang**,* University of California, Los Angeles **INVITED**

PLEASE SEND US AN ABSTRACT. Thank you.

2:40pm **SC+EL+SS-WeA3 Critical Behavior of Epitaxial Si@sub 1-x@Ge@sub x@/Si(001) Islands***, **R.A. Budiman**, H.E. Ruda, D.D. Perovic, B. Bahierathan,* University of Toronto, Canada

We study the island size distributions of three-dimensional Si@sub 1-x@Ge@sub x@/Si(001) islands of varying Ge fractions (x = 0.4-0.7) and thicknesses grown by ultrahigh vacuum chemical vapor deposition. The size distributions of the percolating islands obey the dynamic scaling hypothesis due to random percolation process, only in the small island limit. Morphologies of the islands strongly suggest a presence of Smoluchowski ripening mechanism, in which islands collide and ripen. We therefore combine random percolation and Smoluchowski ripening to analyze the size distributions. To understand the critical behavior of the islands as exhibited by their size distributions, we formulate a mean-field theory of coherently strained island formation by incorporating surface energy and strain relaxation. The resulting phase diagram shows that the island formation in Si@sub 1-x@Ge@sub x@/Si(001) is located near the critical region. Order parameter fluctuations can be estimated by calculating the curvature energy for such a system and we find that the strain fluctuation is indeed relevant to properly describe the island formation in the Si@sub 1-x@Ge@sub x@/Si(001) system.

3:00pm **SC+EL+SS-WeA4 Growth of Coherent Three-dimensional Si Islands on Ge(111)***, **A. Raviswaran**, C.P. Liu,* University of Illinois, Urbana-Champaign*; J.M. Gibson,* Argonne National Laboratory*; D.G. Cahill,* University of Illinois, Urbana-Champaign

We study the evolution of three-dimensional islands during Si/Ge(111) epitaxy. The strain due to lattice mismatch (4.2% tensile) and the difference in the surface energies (@gamma@@sub Si@>@gamma@@sub Ge@) contribute to the formation of the three-dimensional Si islands. We grow Si islands on pseudomorphic Si@sub 0.15@Ge@sub 0.85@ buffer layers (deposited on Ge(111) substrates) in the temperature range 500°C - 650°C using MBE; the (111) orientation is used because the critical thickness of Si layers on Ge(111) is larger than that on Ge(001). We characterize the morphology and relaxation of the Si islands using ex situ AFM, TEM and SEM. Islanding occurs at 1 BL Si coverage, i.e., without the formation of a wetting layer. We observe high densities (~ 10@super 12@ cm@super -2@) of coherent, circular base islands for growth temperatures 500°C - 600°C and low Si coverage (< 2 BL Si). The density and shape of the islands is insensitive to the growth temperature. Beyond a critical width the islands relax plastically, by the nucleation and glide of misfit dislocations; this critical width is ~ 16 nm at 550°C and ~ 25 nm at 600°C. We observe large, incoherent, irregularly shaped islands at higher temperatures (> 600°C) and coverages (> 4 BL Si). As the islands transform from coherent to incoherent, coarsening occurs which results in an increase in the island width and a reduction in the island density. The high temperature (> 600°C) growths show a secondary maximum in the island density near 4 BL Si coverage.

3:20pm **SC+EL+SS-WeA5 Adatom Assisted Stabilization of Ad-dimers on Ge(001)***, **E. Zoethout**, H.J.W. Zandvliet, B. Poelsema,* University of Twente, The Netherlands

Studies of the early stage of near room temperature growth of silicon on Ge(001) have revealed an inconsistency between experimental@footnote 1@ and theoretical@footnote 2@ work. Experimentally a stable cluster has been labeled to be a trough dimer oriented perpendicular to the substrate dimer bonds (D-dimer). The same type of cluster is found in the early stage of near room temperature homoepitaxial growth on Ge(001). Theoretically such a D-dimer is predicted to be energetically unfavorable. It turns out that the apparent D-dimer is actually comprised of three rather than two atoms. The three-atom cluster of Ge or Si on Ge(001) is shown to differ from a trough dimer orientated along the substrate dimer bonds, from a small epitaxial island and also from a three-atom Si cluster on Si(001). The three-atom cluster of Ge or Si on Ge(001) is composed of an ad-dimer in the D-configuration and an adatom on the neighboring substrate dimer row. @FootnoteText@ @Footnote 1@W. Wulfhekel, B.J. Hattink, H.J.W. Zandvliet, G. Rosenfeld, and B. Poelsema, Phys. Rev. Lett. 79, 2494 (1997). @Footnote 2@S.V. Khare, R.V. Kulkarni, D. Stroud and J.W. Wilkins, Phys. Rev. Lett. 60, 4458 (1999).

3:40pm **SC+EL+SS-WeA6 C Incorporation during the Growth Of Ge@sub 1-y@C@sub y@/Ge(001) from Hyperthermal Beams***, **J. D'Arcy-Gall**, D. Gall, P. Desjardins, I. Petrov, J.E. Greene,* University of Illinois, Urbana

C-containing group-IV semiconductor alloys are of interest due to the potential they offer for both band gap and strain engineering in microelectronics. This investigation focuses on the effects of incident particle energy and film growth temperature T@sub s@ on the distribution of C lattice configurations in Ge@sub 1-y@C@sub y@ epitaxial layers grown on Ge(001) from hyperthermal beams obtained by ultra-high vacuum ion-beam sputtering using Kr@super +@. All Ge@sub 1-y@C@sub y@ (y @<=@ 0.03) layers, grown at T@sub s@ = 245-415 °C, are fully-coherent and free of extended defects as judged by high-resolution x-ray diffraction, reciprocal lattice mapping, and transmission electron microscopy. The strain-state of epitaxial Ge@sub 0.99@C@sub 0.01@ alloys grown at T@sub s@ = 300 °C changes from in-plane tension to compression as the Kr@super +@ energy E@sub Kr@ is increased from 300 to 900 eV. This results from an increasing fraction of C incorporated in Ge-C split interstitial sites as a result of the trapping, by substitutional C, of Ge self-interstitials formed due to irradiation by the increasing fraction of sputtered Ge atoms in the high energy tail of the energy distribution. These results are supported by TRIM simulations which show that the number of displaced lattice atoms per incident hyperthermal Ge increases from 0.10 with E@sub Kr@ = 300 eV to 0.24 at 900 eV, and ab initio calculations of layer strain for different C lattice configurations. All Ge@sub 1-y@C@sub y@ alloys grown at E@sub Kr@ = 900 eV are in a state of in-plane compression, which decreases with increasing T@sub s@. Raman scattering results show that the substitutional C concentration in these layers is negligible. Comparison of experimental results with ab initio calculations reveals that an increasing fraction of C incorporates as C pairs as T@sub s@ is increased due to the higher C-C encounter probability on the growth surface.

4:00pm **SC+EL+SS-WeA7 Growth and Characterization of Metastable Ge@sub1-x@C@subx@ Thin Films on Si(100) Substrate.***, **W. Li**, D. Guerin, S.I. Shah,* University of Delaware

The Ge-C system is of interest due to the possibility of band gap engineering on Si. For strain free deposition of Ge@sub1-x@C@subx@, a carbon concentration in excess of 10% is required, assuming that the system obeys Vegard's law. The maximum equilibrium solubility of C in Ge, however, is only 10@super8@/cm@super3@. Molecular beam epitaxy and chemical vapor deposition have been used to grow metastable Ge@sub1-x@C@subx@ thin films with x up to 2.5%. We have used a bias assisted sputter deposition using Ge and C magnetrons to obtain the epitaxial Ge@sub1-x@C@subx@ films with extended carbon solubility. Without any applied substrate bias and C flux, a Ge epitaxial layer on Si(100) substrate was obtained at 750°C with proper substrate preparation. Based on the results of pure Ge epitaxy, C was systematically added. Without the substrate bias, x-ray diffraction analyses show that the films were polycrystalline. With the application of a substrate bias, we were able to obtain epitaxial Ge@sub1-x@C@subx@ films. The Ge (400) XRD peak shifts to higher 2@theta@ were observed indicating C incorporation in the Ge lattice. Extended x-ray absorption fine structure (EXAFS) analyses confirmed that the C was indeed incorporated on the substitutional sites in the Ge lattice. C concentration was determined from XRD, X-ray photoelectron spectroscopy (XPS) and Rutherford backscattering spectroscopy (RBS). A C concentration of up to 5 at.% was obtained. Depth profiles of samples by XPS show that carbon is uniformly distributed in the film. Experiments are underway to study the effects of bias and thickness on the epitaxial deposition of Ge@sub1-x@C@subx@ with even further extension of the concentration of substitutionally situated C in germanium lattice.

4:20pm **SC+EL+SS-WeA8 Electrical and Optical Properties of Silicon : Germanium Alloys prepared by DC Magnetron Sputtering***, **A. Subrahmanyam**, S. Karthikeyan, J. Asbalter,* Indian Institute of Technology, Madras, India*; P. Amirtharaj,* National Institute of Standards and Technology

The Silicon: Germanium (Si:Ge) alloys are being used in various semiconductor devices. As is well known, these alloys offer advantages in band gap engineering, and can integrate well with the existing silicon technology. Several studies have been made on these alloys. In the present paper, we report the electrical and optical properties of Si:Ge alloys prepared by DC Magnetron sputtering technique. A 7.5 cm diameter circular magnetron cathode has been designed and fabricated. The balanced magnetron cathode is operated at low pressures (4.0 x 10@super -3@ mbar). Argon is the sputter gas. The target is prepared by bonding commercially available Silicon wafer to the water cooled copper backing plate. A small portion of the erosion area on the magnetron cathode is covered with pure germanium wafer. The alloys of Si:Ge (undoped) are prepared (at room temperature 25°C) on glass and Si substrates. The growth parameters in the present study are : flow rate of argon (180 - 250 sccm), Magnetron power (80 - 225 watts) and germanium content in the alloy. The thickness and refractive index of the films is measured by ellipsometer in the wavelength range 300 - 700 nm. The thickness of these alloy films is about 150 nm. The alloy films have been found to be amorphous. The germanium content in the alloy films is varied between 15 - 30 atomic % and is estimated by EDAX and RBS analysis. The optical absorption and photo conductivity measurements have been made on these alloys. The optical band gap of these alloys is in the range 1.45 - 1.6 eV. The dark conductivity is in the order 10@super-@ mho cm@super-1@. The deposition rate is observed to be linear with the magnetron power till 120 watts.

4:40pm **SC+EL+SS-WeA9 Preparation and Characterization of Highly Li-doped a-Se Alloy Films for Thermal Neutron Detectors***, **K.C. Mandal**, B. Dille, R.D. Rauh,* EIC Laboratories, Inc.*; A. Burger,* Fisk University*; R.N. Bhattacharyya,* National Renewable Energy Laboratory

This paper describes our recent research in developing highly Li-doped a-Se alloys and thin films for thermal neutron detector applications. The grown Li-doped (35 a/o) a-Se alloy thin films have shown high promise for this application due to the presence of Li in high concentrations, high dark resistivity (2x10@super 14@@ohm@. cm), good charge transport properties (mu-tau@sub e@ = 3.2x10@super -6@ cm@super 2@/V), low cost and relatively easy scale up. Highly Li-doped a-Se alloy has been synthesized in controlled ambient and used for making large area films up to 4x4 sq. inch. The vacuum evaporated a-Se alloy films have been characterized by X-ray diffraction (XRD), atomic absorption (AA), differential thermal analysis (DTA), Raman spectroscopy and X-ray photoelectron spectroscopy (XPS). The detectors fabricated from these films have demonstrated potential for thermal neutron detection for the first time. Details of various steps involved in detector fabrication and testing of these devices will also be presented.

5:00pm **SC+EL+SS-WeA10 Instability in Atomic Step Morphology during the Sublimation of Si(111)***, **Y. Homma**, P. Finnie,* NTT Basic Research Laboratories, Japan

A morphological instability has been predicted to occur during step-flow crystal growth.@footnote 1@ Recently we experimentally demonstrated transitions between stability and instability@footnote 2@ during epitaxial growth on an ultra-flat Si(111) terrace - a terrace which is atomically flat on a 100 µm scale. In this paper, we show that such instability can also occur during step-flow sublimation at high temperatures. Step motion due to sublimation was tracked with in situ scanning electron microscopy. When the size of a terrace becomes comparable to the adatom diffusion length, a new step is nucleated, forming the edge of a new, monolayer-deep crater at the center of an ultra-flat terrace. As a result of successive expansion and nucleation, steps become distributed in a concentric circular pattern. The spacing between steps can be controlled by varying the annealing temperature. When the spacing is less than about 20 µm, the innermost step is typically smooth and nearly circular. For larger spacings, the innermost crater is irregularly shaped while it is still relatively small. The crater becomes smoother as it expands. The instability is manifest when the width of the lower terrace is much smaller than that of the upper terrace. Since the adatom flux from a step to a neighboring terrace depends on the terrace width, by reducing the size of the stabilizing terrace the instability can be initiated. The behavior of a subliming surface is thus similar to that of the growing surface. @FootnoteText@ @footnote 1@ G.

S. Bales and A. Zangwill, Phys. Rev. B 41 (1990) 5500 @footnote 2@ P. Finnie and Y. Homma, Phys. Rev. Lett. to be published.

Surface Science
Room 208 - Session SS1+MC-WeA

Oxide Surfaces, Interfaces and Defects

Moderator: R.L. Kurtz, Louisiana State University

2:00pm **SS1+MC-WeA1 Metal/Metal-Oxide Interactions and Structures in Bulk Truncated and Thin Film Systems --The Theoretical View*, D.R. Jennison,*** Sandia National Laboratories **INVITED**

Using DFT with up to hundreds of atoms per slab unit cell, I use several sources to illustrate basic principles concerning metal-oxide surfaces, interactions with adspecies and metal overlayers, and ultrathin (<1nm) oxide films on metals and adsorption thereon: 1) Metal oxides vary greatly in relaxation to adsorbates, with those of alumina among the largest. This surface becomes so locally oxidizing that multiply charged metal adatoms can occur. 2) The interface between an oxide film and a basal-plane metal substrate can differ fundamentally. Most metals prefer O(1x1), but the nobel metals prefer cations, which convert to a somewhat positive metallic layer with O-ions above. 3) Point defects can nucleate metal islands and alter growth and adhesion. However, common Fs and Vs centers destabilize metal dimers (the first step in nucleation), while another common defect, ad-OH, does the opposite. In fact, 1/3 ML of ad-OH on sapphire reverses the growth mode and more than doubles the adhesion of Cu metal. These results are simply due to geometry and electrostatics. 4) Ultrathin film adsorbate response depends on the substrate: While alumina on Ru is rather inert to a Pd overlayer, the film on Al(111) reacts strongly, drawing substrate metal into the oxide and extruding Al from the top to form a Pd/Al interface. Such is explained by cohesive energy differences between Al and Ru. 5) While complex mixed structures of oxides and metals cannot be predicted by simulation, proposals from STM data can be tested. In addition, model calculations expose basic factors such as interface preference, near-interface oxide film structure, and the resulting film stress, explaining the presense and variety of relief mechanisms. In this active field, examples, including experimental results, are drawn from alumina, magnesia, and titania. My valued collaborators are several. @footnote 1,2@ @FootnoteText@ @footnote 1@www.sandia.gov/surface_science/drj/. @footnote 2@Supported by US DOE.

2:40pm **SS1+MC-WeA3 Ultrathin Fe Oxides on Cu(001): a Search for Half-Metallic Films*, R.H. Madjoe,*** *A.N. Koveshnikov,* Louisiana State University*; J. Karunamuni,* University of South Carolina*; R.L. Stockbauer, R.L. Kurtz,* Louisiana State University

Half-metallic oxides such as CrO2 and Fe3O4 may provide opportunities for new magnetic devices since their single spin orientation at the Fermi level gives rise to spin-dependent transport. However, these films are most often grown on oxide substrates which are not currently incorporated in GMR devices. We report a study of the electronic and geometric structures of Fe3O4 films grown on copper, which is currently used in commercial heterostructures. A broad array of techniques including ARUPS, NEXAFS, LEED and STM were used to characterize these films. They were grown by depositing Fe on Cu(001) at room temperature and oxidizing at 810K in 10-6 Torr O2 ambient. The particular oxide phase that forms depends on the initial Fe thickness. For Fe films less than 2 ML thick, LEED and STM measurements show that oxidation produces an FeO(111) bilayer. The oxide forms long, narrow strips with two mutually-perpendicular orientations aligned along Cu[110] and [110]. Oxidation of thicker Fe layers give crystallites of Fe3O4(111) of micron dimensions, which are oriented 15Â° from the [010] directions and highly lattice-matched to the Cu substrate. Both core level and valence band photoemission data will be presented. Difference spectra show that the interfaces of these films have a metallic density of states at EF, unlike any of the bulk phases of iron oxide. Near-edge x-ray absorption fine-structure (NEXAFS) at both the oxygen K- and Fe L2,3-edges will be presented in addition to magnetic linear and circularly-polarized dichroism (MLD, MCD) data. These data will be discussed in the context of the evolution of the electronic structure to that of thicker bulk-like oxide films.

3:00pm **SS1+MC-WeA4 Low Temperature Microcalorimetric Heats of Adsorption and Sticking Probabilities of Metals on Oxide Surfaces*, D.E. Starr*,** *C.T. Campbell,* University of Washington

Single crystal adsorption microcalorimetry is a powerful method to study the heats of adsorption of gaseous atoms or molecules onto single crystal surfaces. The technique has been utilized to study the energetics of metal film growth from the initial stages of growth through the multilayer regime. Results for metal deposition onto metal oxide substrates all indicate an initial heat of adsorption much lower than the bulk heat of sublimation of the metal. This indicates a weaker interaction of the metal atoms with the substrate than with themselves, providing insights into the energetic driving force for the three dimensional islanding of the metal film in the submonolayer regime. Recent advances in this technique has allowed the first low temperature measurements (~ 160 K) to be performed. Low temperature results for the deposition of Pb onto a MgO(100) thin film grown on Mo(100) will be presented. These measurements have similar sensitivities to room temperature measurements. The changes in the heat of adsorption versus coverage from room temperature measurements to low temperature result from the kinetic factors governing the film morphology. In conjunction with the calorimetric measurements, the metals sticking probability as a function of coverage at a variety of temperatures allows kinetic parameters to be extracted from the model fit to the sticking probability curves. This results in deeper insights into the microcalorimetrically measured heats of adsorption.

3:20pm **SS1+MC-WeA5 Electronic Structure of Grain Boundaries in TiO2 from Ab-Initio Calculations*, Z. Mao*,** *S.B. Sinnott, E.C. Dickey,* The University of Kentucky*; R.F. Wood,* Oak Ridge National Laboratory

It is well known that the properties of grain boundaries have important effects on the electronic and chemical properties of polycrystalline materials. In this work, we apply first principles electronic structure calculations to study the structure of TiO@sub 2@ grain boundaries and compare the results to experimental data. Specifically, the density functional method within the local density approximation is used to determine the structure of several tilt grain boundary structures in TiO@sub 2@. In addition, intrinsic defect formation energies at these boundaries are calculated by examining the stability of various individual defects within the bulk and at the grain boundary. These results provide information about the atomic basis for grain boundary space charge segregation and its dependence on grain boundary structure. This work is supported by the National Science Foundation (DMR-9976851).

3:40pm **SS1+MC-WeA6 Surface Defects on MgO Thin Films: Formation, Detection, Electronic and Chemical Properties*, A.A. Kolmakov*,** *X. Lai, J.A. Stultz, D.W. Goodman,* Texas A&M University

Surface defects play a significant role on metal oxide surfaces since they determine its electronic structure, chemical reactivity and adsorbate kinetics. There is great interest in studying surface defects on thin-film metal oxides to understand the properties of supported catalysts and gas sensing devices at the molecular level. Because of the low density of these oxide defects and sample charging, experimental studies of oxide surface defects still remain a challenging task. Using an ultrathin film deposition methodology and high surface sensitive capabilities of metastable impact electron spectroscopy (MIES), ultraviolet photoelectron spectroscopy (UPS) and temperature programmed desorption (TPD) along with scanning tunneling microscopy (STM), the properties of surface and near-surface defects were probed. A comparative study of morphology and electronic structure with reactivity of low-defect MgO(100) films was undertaken. Defect-ridden films exhibited occupied levels located ~2 eV above the top of the valence band, observed as a separate band in MIES, unlike defect-free thin films. This additional feature was attributed to the emission of electrons from point defects (F-centers) created on the surface and subsurface regions. Initially unseen in MIES, extended defects became detectable via NO titration. These defects manifest themselves as strong, reactive centers. MIES and TPD data indicate that at ~100 K, NO adsorbs dissociatively on surface defects and produces N@sub 2@O. Differences in electronic and chemical properties between these two films were further evidenced from their morphological differences as observed by STM.

4:00pm **SS1+MC-WeA7 Metallic Electronic States on SrTiO@sub 3@ (110) Surface -- An In Situ Conduction Measurement***, **H. Bando**,* Electrotechnical Laboratory, Japan*; Y. Ochiai,* Ibaraki University, Japan*; Y. Aiura,* Electrotechnical Laboratory, Japan*; Y. Haruyama,* Himeji Institute of Technology, Japan*; T. Yasue,* University of Tsukuba, Japan*; Y. Nishihara,* Ibaraki University, Japan

In our previous works we detected metallic electronic states on the SrTiO@sub 3@ (110) surface after annealing in ultra high vacuum (UHV) at relatively low temperature, @<=@ 800 °C, based on a sharp Fermi edge detected by ultraviolet photoemission spectroscopy and finite zero-bias differential conductance by scanning tunneling spectroscopy. In order to verify the metallic feature of the surface as a macroscopic property, electric conductance is measured in situ. For the measurement, a sample holder is designed which enables both annealing in UHV by electron beam and 4-probe electric conduction measurement with uniform electric field. Conductance contributed by bulk is separated by measuring the decrease of total conductance by adsorption of oxygen at room temperature, which is supposed to modify only the surface electronic states. Surface conductance is deduced between 150 K to 300 K and showed a metallic feature. Comments will be presented on the effects of surface anisotropy and photo-induced carriers. Moreover, the surface conductance during exposure to oxygen is monitored in situ, and showed a reversible-like change depending on the oxygen pressure. This possibly evidences that the oxygen molecules which temporarily stay on the surface suppress the conduction by surface electrons.

4:20pm **SS1+MC-WeA8 First-Principles Calculations on Al@sub 2@O@sub 3@/TiC Growth and Interface***, **C. Ruberto**, B.I. Lundqvist,* Chalmers University of Technology and Göteborg University, Sweden

First-principles calculations based on density-functional theory are performed to understand the first steps in the growth of alumina on TiC(111). The alumina/TiC interface is theoretically very interesting, being an example of interface between an oxide, ionic and insulating, ceramic and a covalent transition-metal ceramic with metallic and ionic character. The TiC(111) facet is furthermore a highly active and polar surface. Technologically, the interface is of high importance in wear-resistant cutting tools used in industrial high-speed applications. Different phases of alumina (mainly the @alpha@ and @kappa@ phases) are used as chemically-inactive coatings on cemented-carbide tools. These coatings are grown on TiC(111), TiN(111), or Ti(C,N)(111) through chemical-vapor deposition (CVD). It is known that the coating quality and phase content are determined by the nucleation on the substrate surface. For example, a region of @gamma@ alumina is sometimes observed between TiC and @kappa@ alumina. This work is the first step towards establishing a fundamental understanding of the interfacial structure and of the growth of alumina on TiC(111). This is done in several steps. We investigate the adsorption energies of the different atomic species present in the CVD reactor on the TiC(111) surface. The energetics for the different atomic configurations of an aluminum layer at 2/3 coverage on TiC(111)-O are studied and the observed structural stability is understood on the basis of bonding character. The influence of thermal lattice expansion is discussed. The stability and bonding character of a layer of stoichiometric Al@sub 2@O@sub 3@ in different structural configurations on TiC(111)-O are then examined. Finally, the structure and stability of all different atomic terminations of the @kappa@-Al@sub 2@O@sub 3@(001) and (00-1) surfaces, the preferred CVD growth direction, are presented and discussed.

4:40pm **SS1+MC-WeA9 Self-Diffusion in Ceria***, **C.L. Perkins**, M.A. Henderson, G.S. Herman,* Pacific Northwest National Laboratory

Ceria, an oxygen storage material vital to the proper functioning of automobile three-way catalysts, is typically viewed as an anion conductor. In light of mounting evidence that in the prototypical oxide rutile TiO@sub 2@ the mobile species are Ti cations rather than O anions, the diffusivities of both cerium and oxygen in ceria were explored via temperature programmed static secondary ion mass spectrometry (TPSSIMS). The 500 Å thick CeO@sub 2@(111) film was heteroepitaxially grown by molecular beam epitaxy on a yttria stabilized zirconia substrate. Although high quality LEED patterns and Auger spectra free of signals from elements other than cerium and oxygen were obtained after just a few sputtering and annealing cycles, further cleaning was necessary to remove intense alkali and alkaline earth signals observed in SSIMS. The CeO@sub 2@(111)surface was slightly enriched in @super 18@O by first annealing the film in UHV at 830 K and then exposing the 130 K crystal to @super18@O@sub 2@. TPSSIMS data in conjunction with temperature programmed desorption (TPD) data demonstrate that surface oxygen begins to diffuse into the bulk around 550 K. Physical deposition in an @super18@O@sub 2@ background of submonolayer amounts of isotopically enriched cerium (@super 136@Ce) allowed the simultaneous study of the diffusivity of both cerium and oxygen. Surface cerium cations were found to be immobile with respect to diffusion into the bulk up to the highest temperature studied, 900 K.

5:00pm **SS1+MC-WeA10 Defect Characterization on MgO(100) Using Adsorption of Small Molecules***, **Z. Dohnálek**, G.A. Kimmel, R.S. Smith, S.A. Joyce, B.D. Kay,* Pacific Northwest National Laboratory

MgO(100) films with controlled defect densities are grown epitaxially on Mo(100). The crystalline order is probed using both low energy electron diffraction (LEED) and the adsorption of small probe molecules such as N@sub 2@, Ar, CO, CH@sub 4@, H@sub 2@O, NH@sub 3@ and CH@sub 3@OH. Significant changes in the LEED beam profiles are observed for films grown at various substrate temperatures, deposition rates, and film thicknesses. Thick films grown at high temperatures yield the sharpest LEED profiles. While the quality of the LEED pattern is related to the presence of morphological defects, it is difficult to quantify and characterize the defects by LEED alone. Temperature programmed desorption (TPD) of physisorbed molecules deposited at 20K reveals a wide distribution of binding sites on the highly-defective films. Analysis of the TPD spectra yields the binding energies and concentrations of these defect sites for various adsorbates. Both the LEED and TPD from the highest quality epitaxial films are indistinguishable from highly-ordered bulk MgO(100). Even on the best surfaces, a well resolved minority desorption channel related to defects is observed, thereby demonstrating the high sensitivity and quantitative nature of TPD in characterizing defects. * Pacific Northwest National Laboratory is operated for the Department of Energy by Battelle under Contract DE-AC06-76RLO 1830.

Surface Science

Room 209 - Session SS2+VT-WeA

Adsorption and Desorption Phenomena I

Moderator: C.M. Friend, Harvard University

2:00pm **SS2+VT-WeA1 The Role of Two-dimensional Compressibility in Physisorption, Competitive Adsorption and Dynamic Displacement***, **G.A. Kimmel**, Z. Dohnálek, R.S. Smith, B.D. Kay,* Pacific Northwest National Laboratory **INVITED**

We have investigated the physisorption of gases (Ar, N@sub 2@, CH@sub 4@, etc) on Pt(111) with modulated beam techniques, beam reflection measurements and temperature programmed desorption (TPD). The kinetics of adsorption and desorption for systems where the coverage is larger than ~0.8 monolayer (ML) is dominated by the two-dimensional compression of the adsorbate layer. In particular, at coverages near 1 ML the repulsive interaction between adsorbates increases causing an approximately linear decrease in binding energy as the coverage increases. The formation of the first monolayer is complete when the binding energy of the adsorbates in the compressed first layer is equivalent to the binding energy of an adsorbate in the second layer (i.e. when the chemical potential of the first and second layers are equal). Evidence for this compression arises in the TPD of physisorbed gases from Pt(111) which reveal a non-zero, nearly constant desorption in the temperature range between the desorption peaks of the "first" and "second" monolayers. Modulated beam experiments also support this interpretation. In that case, the Pt(111) surface is pre-covered with ~1 ML of gas and then exposed to gas pulses of varying duration (~0.05 s - 1.0 s) and the desorbed/reflected flux is monitored. Another example where the two dimensional compression of the adsorbate layer is important occurs when the "competitive" adsorption of two gases is examined. In these experiments, an adsorbate can be displaced/desorbed when the surface is exposed to a gas which has a higher binding energy to the substrate. We will present a simple model for the binding energy as a function of coverage which explains the observed adsorption/desorption kinetics for a variety of systems.

2:40pm **SS2+VT-WeA3 Molecular Adsorption and Growth of n-butane Adlayers on Pt(111)***, **J.F. Weaver**,* University of Florida*; M. Ikai, A. Carlsson, R.J. Madix,* Stanford University

The molecular adsorption of n-butane and the growth of n-butane adlayers on Pt(111) have been investigated using molecular beam techniques, temperature-programmed desorption and low-energy electron diffraction. Our results indicate that four adlayer phases develop sequentially as the n-butane coverage increases from the submonolayer to second layer ranges at surface temperatures near 98 K. The structural properties of the adlayer and the kinetics for adlayer growth will be discussed in detail. Interestingly, although the changes in adlayer structure significantly affect the rates of n-butane desorption and surface diffusion, the adsorption probability of n-butane on Pt(111) is found to increase smoothly with increasing coverage. This finding indicates that the long-range arrangements and orientations of molecules in the n-butane adlayer have a negligible influence on the intrinsic adsorption dynamics, suggesting that the energy transfer processes that facilitate adsorption are highly localized.

3:00pm **SS2+VT-WeA4 Optical Effects of Monolayer and Multilayer Adsorption: Formic Acid and Methanol on Cu(100)***, **C.-L. Hsu**, E.F. McCullen, R.G. Tobin,* Tufts University

We have studied the adsorption of formic acid (HCOOH) and methanol on epitaxial Cu(100) films at 125 K in both the monolayer and multilayer regimes, using infrared reflectance and dc resistance measurements and visible-light ellipsometry. The results are analyzed using an electron scattering model for reflectance changes due to chemisorbed monolayers, and a macroscopic three-layer model for physisorbed multilayers. For methanol, which is only physisorbed on Cu, the infrared reflectance increases linearly with film thickness (determined ellipsometrically) in agreement with the three-layer model. For formic acid the first monolayer is chemisorbed and scattering of conduction electrons from the adsorbates leads to an initial decrease in reflectance, together with an increase in the electrical resistance of the Cu film. At higher formic acid exposures physisorbed multilayers form, leading to a reflectance increase similar to that observed for methanol. This behavior is qualitatively consistent with expectations, but there are some surprising features. As formic acid exposure increases, the initial reflectance drop continues even after the resistance change is largely complete, even though both effects are believed to result from the same process. The subsequent rapid rise in reflectance suggests that the sticking coefficient is much lower for the first layer than for subsequent layers. Possible explanations for these effects will be discussed.

3:20pm **SS2+VT-WeA5 Precursor-mediated Dissociation and Trapping Desorption of Oxygen on Cu(001)-2@sr@2x@sr@2-O***, **M. Yata**, Y. Saitoh,* National Research Institute for Metals, Japan

The adsorption and desorption of oxygen on Cu(001)-2@sr@2x@sr@2-O has been studied by molecular beam method. Angular and time-of flight distributions have been measured for scattering oxygen from the surface. The time-of flight distributions can be fitted by nonshifted Boltzmann distributions. This means that the oxygen molecules are trapped at the surface in a precursor state and subsequently desorb from the surface. The translational temperature of the desorbing oxygen is lower than the surface temperature, which suggests that there is no barrier for desorption from the precursor state. The dissociative sticking probability of oxygen increases as the translational energy of incident oxygen decreases. This probability also increases with increasing surface temperature. These results suggest that the adsorption of oxygen on the Cu(001)-2@sr@2x@sr@2-O surface proceeds via a precursor-mediated dissociation process rather than by a direct activation process. This is contrast to the dissociative adsorption of oxygen on clean Cu(001) in which the dissociation occurs by direct collisional activation. There exists a competition between dissociation reaction and desorption once the oxygen molecule is trapped in the precursor state. We have estimated the difference in activation energies between the dissociation and desorption of 330 meV. The effect of tensile stress on the dissociative adsorption reaction of oxygen on the Cu(001)-2@sr@2x@sr@2-O surface will be also discussed.

3:40pm **SS2+VT-WeA6 The Effect of Deposition Pressure on Adsorbate Structure and Coverage: Oxygen on W(110)@footnote 1@***, D.E. Muzzall,* University of California, Davis*; C.S. Fadley,* University of California, Davis and LBNL*; **S. Chiang**,* University of California, Davis

In most prior surface science studies, it has been assumed that total exposure, rather than pressure and time as independent variables, controls the types of adsorption structures formed. The importance of deposition pressure as a variable, however, was recently suggested in a study of the kinetics of the low pressure adsorption of oxygen on W(110) using X-ray photoelectron spectroscopy (XPS)and diffraction.@footnote 2@ As a more quantitative measure of such effects, we have used ultrahigh vacuum scanning tunneling microscopy (STM), low energy electron diffraction (LEED), and XPS to explore the adsorbate structures and the coverage dependence of O/W(110) as a function of deposition pressure at room temperature. For the same total adsorbate exposure in Langmuirs (L), we find that changes in deposition pressure of as little as a factor of 3 cause significant changes in the apparent structures, domain sizes (e.g., of (1x2)O), and adsorbate coverage in monolayers. Total coverages derived from STM data using a software thresholding technique indicate that a critical dosing pressure exists for both the (2x1) and (2x2) structures, 1 x 10@sup -9@ and 3 x 10@sup -9@ torr respectively, below which coverage does not increase with increasing exposure time. This indicates that an equilibrium condition has been reached, from which surface free energies for both of these structures can be derived.@footnote 3@ Finally, in addition to the ordered (1x2), (2x2), and (1x1) structures for O/W(110), we have characterized a new fourth ordered structure by LEED and STM. The structure formed for oxygen exposure of 3 to 6 L and coexisted with the (1x2) structure. The primitive unit cell is a rectangle, 0.77nm x 1.37nm, with 15 W and 6 O atoms and has the matrix notation ((3,-1),(0,5)) relative to the W(110) substrate. @FootnoteText@ @footnote 1@ Supported by NSF DMR-9522240. @footnote 2@ Y. X. Ynzunza et al, Surf. Sci., in press. @footnote 3@ P. Liu et al, Surf. Sci. 417 (1998) 53.

4:00pm **SS2+VT-WeA7 STM Investigation of Benzene Adsorption on Ag(110)***, **K.F. Kelly**, J.J. Jackiw,* Pennsylvania State University*; J.I. Pascual, H. Conrad, H.-P. Rust,* Fritz Haber Institute, Germany*; P.S. Weiss,* Pennsylvania State University

We have investigated the adsorption of benzene on Ag(110) using the scanning tunneling microscope. We found that the molecules preferentially adsorb above step edges at 66 K. The preference for step edge adsorption is attributed to the Smoluchowski effect enhancing the empty states to which charge is donated from the @pi@ orbitals of the benzene. However, there is no adsorption at the [001] steps. A lack of free charge due to a gap in the Ag Fermi surface along that direction reduces the Smoluchowski effect and thus the adsorption at these steps. After further deposition at 4 K, we find that benzene forms a weakly adsorbed hexagonal monolayer. The monolayer is imaged at large tip-sample separations and is transparent upon closer approach. The interaction of benzene molecules with steps and point defects reduces this transparency.

4:20pm **SS2+VT-WeA8 Scanning Tunneling Microscopy and Spectroscopy of Metal Tetraphenylporphyrins on Au(111)***, K.W. Hipps,* ***D.E. Barlow**, L. Scudiero,* Washington State University

STM images of metal(II) tetraphenylporphyrin monolayers on Au(111) are presented for several transition metal ions. The constant current images clearly reflect the electronic nature of the metal ion used. Scanning tunneling spectroscopy (dI/dV curves) also allows one to differentiate between the metal complexes. The primary electroactive states, as shown by tunneling spectroscopy, are those involving both occupied and unoccupied molecular orbitals close to the Fermi energy of the Au(111) substrate. Scanning tunneling spectroscopy results for the negative sample bias region are compared to Ultra-violet photoelectron spectra of these same compounds on Au.

4:40pm **SS2+VT-WeA9 Theory of Oxygen Adsorption on Ag(111): A DFT-GGA Investigation***, W. Li,* Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany*; **C. Stampfl**,* Northwestern University*; M. Scheffler,* Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany

O/Ag(111) is an important system with unique catalytic behavior for several large-scale industrial processes, e.g., ethylene epoxidation and partial oxidation of methanol to formaldehyde. In spite of its importance, very little is known about the behavior of O at Ag(111) (which depends sensitively on pressure and temperature) on the microscopic level, and the precise atomic location and chemical nature of the various O species that form, e.g. on-surface, subsurface, in-surface. Using density-functional theory within the generalized gradient approximation, we investigate the interaction between oxygen and Ag(111). We found that the interaction between silver and oxygen is very weak. Adsorption becomes unfavorable for coverages between 0.33 and 0.50, with respect to the gas molecule O@sub 2@. Compared to hcp site, the fcc site is preferable, and the difference in adsorption energy differs by less than 0.17 eV/atom for the whole range of coverage considered. Strong charge transfer from silver to oxygen has been found due to the large difference in electronegativity between oxygen and silver, and results in a significant change in work function, which increases monotonically with oxygen coverage. Experimental studies report that at elevated temperatures two ordered phases form: a (4x4) structure (T@>=@400K),@footnote 1@ and a high-temperature (@sr@3 x @sr@3)R30° (T@>=@800K)@footnote 2@ structure. With respect to the latter, a surface substitutional site has been proposed. Our results show that this structure is unfavorable. For subsurface adsorption we find that oxygen prefers the octahedral site, but at coverage 0.33 it is also endothermic with respect to free O@sub 2@. We discuss alternative geometries for this phase. @FootnoteText@ @footnote 1@ G. Rovida et al., Surf. Sci. 43, 230 (1974); C. I. Carlisle et al., Phys. Rev. Lett. 84, 3899 (2000). @footnote 2@ B. Pettinger et al., Phys. Rev. Lett. 72, 1561 (1994); X. Bao et al. Phys. Rev. B 54, 2240 (1996).

5:00pm **SS2+VT-WeA10 Adsorption of Propylene on Clean and Oxygen Covered Au(111) and Au(100)***, **K.A. Davis**, D.W. Goodman,* Texas A&M University

The adsorption of propene on Au(111) and Au(100) was investigated using temperature programmed desorption (TPD) and high resolution energy loss spectroscopy (HREELS). A desorption activation energy of 9.4 kcal/mol and very small (< 25 cm@sup -1@) shifts of the vibrational frequencies from their gas phase values indicate that the interaction of propene with the surface is weak. Energy loss spectra suggest that propene adsorbs with its molecular plane tilted slightly with respect to the surface plane. Atomic oxygen, chemisorbed on the gold surfaces, was characterized using TPD and low energy electron diffraction (LEED), and its interaction with propene investigated. HREEL spectra of propene on the oxygen covered surfaces show shifts in the intensities and frequencies of the -CH@sub 2@ related vibrational features. Small amounts of product with masses 56 and 58 amu were observed for propene adsorbed onto a 0.4 ML oxygen-covered surface.

Surface Science
Room 210 - Session SS3-WeA
Surface and Interface Structure I

Moderator: B.P. Tonner, University of Central Florida

2:00pm **SS3-WeA1 Adsorbate Structure Determination on Surfaces using Normal-Incidence X-ray Standing Waves***, **D.P. Woodruff**[1],* University of Warwick, UK **INVITED**

X-ray standing waves (XSW) provide a particular simple way of obtaining quantitative information on adsorption geometries on well-characterised surfaces, and working a normal incidence (NIXSW) to the Bragg scatterer planes offers some specific advantages. In particular, under these conditions the experiment is extremely tolerant of crystal mosaicity and can be applied routinely to metal crystals. Normal incidence also implies lower photon energies, typically around 3 keV, making photoemission detection of the photoabsorption straight-forward. Photoemission detection offers two important advantages, namely easier access to low atomic-number species, and the possibility of obtaining chemical-state specific structural information through the use of 'chemical shift' in the photoelectron binding energies. On the other hand, photoemission detection requires the use of a modified interpretational scheme to take account of non-dipole effects in the angular dependence of the photoemission. These various aspects of the technique will be illustrated with recent results including: the direct measurement of non-dipole angular parameters; the use of chemical-shift NIXSW to determine the local geometries of coadsorbed molecular fragments (e.g. PF@sub 3@ species produced by X-ray fragmentation on Ni(111) and CH@sub 3@SH, CH@sub 3@S- and S on Cu(111) following surface reaction), and determinations of the temperature-dependent local structure of CO adsorbed on Ni(111).

2:40pm **SS3-WeA3 Oriented Quantum Dots By Buffer Layer Growth Process***, **A.P. Baddorf**, J.F. Wendelken,* Oak Ridge National Laboratory*; C.T. Venkataraman, T. Gog,* Argonne National Laboratory

Quantum dots of Fe formed by a multi-step growth process are shown to be highly oriented on a Cu(100) substrate. Growth involved deposition of Fe on a buffer of 200 layers of condensed Xe. The Xe buffer layer, which promotes clustering, was subseque ntly removed by heating. In situ scanning tunneling microscopy results reveal formation of 3-D Fe clusters averaging 10 nm in diameter. An additional 20 nm thick cap of Cu was deposited over the Fe to allow ex situ x-ray studies at the Advanc ed Photon Source. Fe clusters were found to be highly oriented, with the close-packed [110] direction normal to the Cu(100) surface and with two in-plane orientations. The first in-plane structure has Fe \{-112\} planes aligned with Cu \{001\} and the se cond has Fe \{-110\} planes aligned with Cu \{001\}. These orientations are not observed in molecular beam epitaxy of Fe directly onto Cu(100) or in precipitate growth. Buffer layer growth bypasses the intermediate fcc Fe phase formed by direct deposition on fcc Cu and brings bcc Fe immediately into contact with fcc Cu. Sidestepping the fcc Fe phase may allow the newly observed orientations.@footnote 1@ @FootnoteText@ @footnote 1@ORNL is managed by UT-Battelle, LLC, under US DOE contract DE-AC05-00OR22725. The APS is supported by US DOE contract W-31-109-Eng-38.

3:00pm **SS3-WeA4 Direct Observations of Ordered Domain Structures and their Dynamics : Pb on Cu(111)@footnote 1@***, **R. Plass**, N.C. Bartelt, G.L. Kellogg,* Sandia National Laboratories

There is considerable scientific interest in the spontaneous formation of two-dimensional periodic domain structures due to long-range interactions in two-phase systems. Theoretical investigations of the stability of periodic structures due to dipolar interactions predict a progression of droplet and striped phases as a function of area fraction@footnote 2@ but experimental verification has been elusive. Using low energy electron microscopy (LEEM), we find that the growth of Pb on Cu(111) reproduces this domain evolution with surprising accuracy. Above 25C, Pb on Cu(111) follows the SK growth mode@footnote 3@ with a disordered surface alloy saturating at 0.4 ML Pb and an incommensurate (incom. hereafter) overlayer covering the surface at 1.0 ML Pb. As Pb deposition proceeds on the surface alloy held at 385C, the density of incom. structure droplets (about 90 nm in diameter) increases steadily. The droplets clearly repel each other, and pack together into a fairly well ordered lattice. They achieve maximum density near 0.3 area fraction (incom.) after which there is an abrupt transition to a striped phase characterized by lengthening bands of surface alloy and incom. regions. The stripes completely cover the surface at 0.5 area fraction, after which another abrupt transition occurs between the striped phase and a conjugate droplet phase where the surface alloy forms droplets in the incom. matrix. The conjugate droplet maximum density is near 0.7 area fraction. The domain structures' spatial dimensions, as well as the size of their thermal fluctuations are temperature sensitive. We use this sensitivity to probe the energetics responsible for the domain structures. @FootnoteText@ @footnote 1@ Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin company, for the U.S. Dept of Energy, contract #DE-AC04-94AL85000 @footnote 2@ K.-O. Ng and D. Vanderbilt, PRB 52 (95) 2177. @footnote 3@ C. Nagl, et al., Surf. Sci. 321 (94) 237.

3:20pm **SS3-WeA5 Normal Incidence X-ray Standing Wave and Medium-energy Ion Scattering Investigation of the Structure of Ultra-thin Films on Cu(111)***, **M.D. Crapper**, M.T. Butterfield,* Loughborough University, U.K., UK

Many of the techniques available for surface structural determination fall into two broad categories. The first of these is the family of diffraction techniques, where long-range order is required to allow investigation of a structure. In samples that are not completely ordered, a diffraction based technique will often preferentially reveal information about the regions of the sample that are ordered. The second category is the so-called local probes, which sample the environment around a particular species but do not reveal information about the long-range order. Two techniques that do not clearly fall into either category, but have aspects of each are medium energy ion scattering (MEIS) and the normal incidence X-ray standing wave method (NIXSW). Both of these methods can yield valuable information where imperfect order is present, but on a scale larger than merely local. We report the novel application of a combination of these methods to investigate the structure of ultra-thin overlayers of Co, Fe and Mn on Cu(111). In the case of Co on Cu(111), pure fcc growth does not continue after the first two layers, but there is no one single growth mode. Instead there is a gradual inclusion of stacking faults with evidence of both hcp and fcc twinning. The initial growth of Fe on Cu(111) is also fcc but with a transition of the entire film to bcc at around 5-8 ML rather than a gradual transition. Overlayers of Mn show no site coherence, even below one monolayer. Upon annealing, however, an alloy is formed to a depth of around five layers that has an effective fcc structure but with increased d-spacing over that found in Cu(111) and with Mn substituting some Cu sites.

3:40pm **SS3-WeA6 Low Energy Dynamics for S/Cu***, **C.J. Hirschmugl**,* University of Wisconsin, Milwaukee*; M.V. Pykhtin, S.P. Lewis,* University of Georgia

Dissociated H@sub 2@S on Cu(100) at 300K has been studied by a combination of AES, LEED, and Far-IRAS in the 200-2200 cm@super -1@ frequency range using synchrotron radiation. Density functional theory (DFT) calculations for a p(2x2) ordered overlayer of S on Cu have also been completed. In the Far-IRAS experiments, diffusive scattering of substrate electrons from the adsorbates gives rise to a broadband infrared absorption. This behavior was induced by sulfur coverages up to and including the p(2x2) overlayer (0.25 monolayers (ML)). DR/R at high frequency (2200 cm@super -1@) changes monotonically with increasing coverage up to 0.125 of a monolayer, and then remains constant. For the

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[1] **Medard W. Welch Award Winner**

low-coverage linear regime, we calculate a scattering cross section @sigma@ of sulfur for the substrate free electrons and the e-hole pair damping rate @eta@ for the S hindered translation. We apply expressions arising from a "friction" model proposed by Persson to determine these parameters from the broadband infrared absorption data. In addition, we determine both @sigma@ and @eta@ for the ordered overlayer from previously published inverse photoemission results and DFT calculations, using a complementary theory proposed by Persson. The scattering cross section for the disordered overlayer (below 0.125 ML coverage of S) is determined to be approximately 20 Å @super 2@ from the infrared results. The scattering cross section for the ordered overlayer is dramatically smaller, approximately 3 Å @super 2@ as determined from both the photoemission results and DFT calculations. The non-linear behavior in the background change for S adsorption is attributed to a changing cross section, or a disorder to order effect.

4:00pm **SS3-WeA7 Does Adsorbed Oxygen Change the Electron Density in Cu?***, **E.F. McCullen**, C.-L. Hsu, R.G. Tobin,* Tufts University

We present new evidence that thin Cu films can have significantly lower conduction electron density n than pure bulk Cu, and that the resistivity increase caused by oxygen adsorption is due in part to a further reduction in n. This finding contradicts the prevailing model of adsorbate-induced resistance, which attributes the resistance increase to electron scattering. In a series of experiments we measured simultaneously the infrared reflectance and dc resistance changes of epitaxial Cu(100) films during oxygen dosing. Earlier experiments challenged the scattering model by showing that the reflectance-resistance change ratio is adsorbate-dependent.@footnote 1@ Adsorbate-induced changes in n could account for the results, but only if n in the films was significantly below the bulk value. The present work shows that the films indeed have reduced electron density. We find that the reflectance-resistance change ratio for adsorbed oxygen depends upon the clean-film conductivity, which varies from sample to sample. This dependence can be understood if the variations in clean-film conductivity are due in part to variations in n. We use these data to set limits on the films' electron density. The results are consistent with a model in which the resistance change produced by oxygen is caused by equal contributions from scattering and reductions in n, and in which each oxygen atom localizes about two conduction electrons. @FootnoteText@ @footnote 1@ E.T. Krastev, D.E. Kuhl and R.G. Tobin, Surf. Sci. Lett. 387, L1051 (1997); C.-L. Hsu, E.F. McCullen and R.G. Tobin, Chem. Phys. Lett. 316, 336 (2000).

4:20pm **SS3-WeA8 Soft X-ray Photoelectron Spectroscopy Studies of Faceting and Alloying for Ultra Thin Films of Ruthenium on W(111) and W(211)***, **G.J. Jackson**,* Rutgers University*; J.E. Rowe,* North Carolina State University*; T.E. Madey,* Rutgers University

High resolution soft X-ray photoelectron spectroscopy (using synchrotron radiation) and low energy electron diffraction (LEED), have been used to study alloying and faceting of Ru dosed onto W single crystal surfaces. W 4f core-level photoemission spectra and valence band spectra have been measured at various photon energies for W(111) and W(211), this photoemission being collected along the surface normal and at shallow grazing angles. The ultrathin film growth and evolution before and after annealing, on both W surfaces, has been investigated for coverages ranging from 0 to greater than 3 physical monolayers. After annealing multilayers of Ru on W(211) at low temperature (600 K), core-level shifts in the W 4f photoemission indicate formation of a Ru/W alloy that may be subsurface. Upon annealing to higher temperatures (600-1600 K), the core-level shifts reveal a concentrated Ru/W alloy. For the W(111) surface, previous studies from several other 4d and 5d dosed metals have shown that the ultrathin film covered surface forms nanoscale pyramidal facets with (211) faces. However, our LEED observations provide no evidence that Ru induces faceting of W(111). W 4f core-level shifts and their relative photoelectron intensities have indicated that clustering may occur on the W(111) surface after annealing. The results from studies of the Ru investigations are closely compared with previous studies from Pt,Pd,Ir,Rh dosed onto W(111) and W(211). In these cases it has been shown that fractional monolayer coverages do not form alloys and that for coverages exceeding 1 ML, the W atoms can dissolve into the adsorbed layer. Our results indicate some differences in the thermal stability of Ru/W, compared with Pt,Pd,Ir, Rh on W.

4:40pm **SS3-WeA9 Oxygen Induced Faceting of Ir(210)***, **I. Ermanoski**, K. Pelhos, T.E. Madey,* Rutgers, The State University of New Jersey

As a part of a larger program to study the morphological stability of adsorbate covered metallic surfaces, we have investigated the adsorption of oxygen on fcc Ir(210) and the oxygen induced faceting of Ir(210). The techniques we used include low energy electron diffraction (LEED), temperature programmed desorption (TPD), Auger electron spectroscopy (AES) and scanning tunneling microscopy (STM). The atomically rough Ir(210) surface, when exposed to more than ~0.9L of oxygen and annealed to temperatures higher than 600K, experiences significant morphological restructuring: pyramid-like structures (facets) are formed on the initially planar surface. Our high temperature LEED measurements show that these pyramidal facets exhibit a quasi-reversible behavior upon annealing to higher temperatures. The surface reverts to its planar state at temperatures above 850K but, provided the maximum annealing temperature is below the desorption temperature of oxygen, facets reappear upon cooling to temperatures below 800K. LEED measurements show that these facets have a different structure than the original ones. Furthermore, we are able to remove the oxygen from the surface via catalytic oxidation of CO at 480K, while preserving the faceted structure. TPD and AES have shown that residual adsorbed oxygen and CO are negligible after this procedure. The faceted clean surface is stable up to 600K, but irreversibly reverts to the planar state when annealed above 600K. These experiments indicate that the clean, faceted, metastable Ir(210) surface provides an ideal substrate to study thermal relaxation of nanometer-scale surface features.

5:00pm **SS3-WeA10 Evolution of Ni(110) Surface with Low Energy Ion Sputtering***, **S.-J. Kahng**, B.-Y. Choi, J.-Y. Park, Y. Kuk,* Seoul National University, Korea

We have studied the spatio-temporal evolution of the Ni(110) surface structure induced by the low energy ion sputtering with scanning tunneling microscopy. In order to have better understanding of the sputtering kinetics, we performed sputtering and homoepitaxial growth experiments at 295 K. In the early stage of sputtering, erosion pits and adatom islands, elongated along the [110], are present with asymmetric adatom kinetics. They become seeds for the ripple structure under the strong diffusion bias along the [001] direction. The surface roughness increases linearly with sputtering time. In the late stage of sputtering, however, symmetric mounds replace the ripple structure and the surface roughness saturates to certain point, showing good agreement with the recent numerical simulation on the basis of nonlinear Kuramoto-Sivashinsky equation.

Thin Films
Room 203 - Session TF+EL-WeA
In-situ Characterization of Thin Film Growth

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

2:00pm **TF+EL-WeA1 Monitoring of Thin Film Metallization by Metastable He Atom Scattering***, **G. Witte**,* Lehrstuhl fuer Physikalische Chemie I, Germany*; P. Fouquet,* Physikalische Chemie I, RUB, Germany

Here we introduce metastable helium atom scattering (MHAS) to characterize metallization transitions occuring during the growth of ultrathin alkali metal (AM) films on metal and semiconductor surfaces. This technique combines the high sensitivity of HAS for measuring coverage and geometrical structure of the adlayer and the extreme surface sensitivity of the metastable atom deexcitation rate to detect modifications of the electronic surface structure.@footnote 1@ In case of Na, K and Cs on Cu(100) an onset of metallization was found at coverages of about half a monolayer. On the other hand for GaAs(110) somewhat larger coverages are required to produce metallic AM films, which are found to grow only below room temperature. These results are in good agreement with previous MDS experiments. Further experiments were carried out for alkali earth metal (AEM) films, where a particular attention is drawn to the comparison of Cs and Ba on Cu(100). It is shown that the onset of metallization for both systems is very similar and can be well described by a 2D Herzfeld model. Finally, MHAS can also be applied to characterize the demetallization of ultrathin AM and AEM films upon adsorption of CO or oxygen.@footnote 2@ @FootnoteText@ @footnote 1@ P.Fouquet and G. Witte, Phys. Rev. Lett. 83, 360 (1999). @footnote 2@ P.Fouquet and G. Witte, Surf. Sci. 454-456, 256 (2000).

2:20pm **TF+EL-WeA2 Ultraviolet Absorption Spectroscopy of Polytetrafluoroethylene Deposition by Pyrolytic CVD***, **B.A. Cruden**, K.K. Gleason, H.H. Sawin,* Massachusetts Institute of Technology

Polytetrafluoroethylene films have been deposited for use low dielectric constant materials in microelectronic chips. Deposition is performed through pyrolysis of hexafluoropropylene oxide (HFPO) to produce CF@sub 2@, which can then polymerize and deposit as a thin film. The variation of CF@sub 2@ concentration as a function of reactor conditions has been characterized by UV Absorption spectroscopy. CF@sub 2@ concentration is observed to go through a maximum with respect to both pressure and pyrolysis temperature when it is present in large amounts (~10@sup 14@ cm@sup -3@). The kinetics known for HFPO cracking and CF@sub 2@ recombination are not sufficient to describe these dependencies. An additional mechanism of particle formation, by CF@sub 2@ insertion into (CF@sub 2@)@sub n@ oligomers, has been introduced to produce a kinetic model for CF@sub 2@ concentration measurements. Deposition rates are seen to qualitatively track with CF@sub 2@ concentration variations. Attempting to develop a specific relationship between CF@sub 2@ concentration and deposition rate yields a sticking coefficient of ~4x10@sup -5@, which is consistent with what has been measured in a CF@sub 2@ beam experiment. However, this result does not adequately describe deposition profiles, and under some conditions, higher deposition rates than this sticking coefficient allows for have been observed. These results point to two important factors. First, under regimes of high CF@sub 2@ concentration, gas phase polymerization can produce species that contribute significantly to deposition. Second, it is possible that other properties of the deposition can affect the sticking coefficient. The final observation of note is that deposition only becomes detectable when CF@sub 2@ concentration approaches its maximum value. This might imply that (CF@sub 2@)@sub n@ species may be responsible for deposition.

2:40pm **TF+EL-WeA3 Near-edge Valence Band Structure of Amorphous Hydrogenated SiC Thin Films by a Combined use of Auger and Photoemission Processes*, M.-H. Lee*,** *F.S. Ohuchi,* University of Washington

Although x-ray photoelectron spectroscopy (XPS) nominally provides useful information about the valence-band (VB) electron density of state (DOS), the VB leading edges for Si-C alloys are not adequately evaluated due to large difference in the photoionization cross-sections between Si-3p and C-2p. A core-valence-valance (CVV) Auger transition contains information about the local valence electronic structure of the probed atom due to the direct coupling of the core and valence levels in the Auger process. In addition, the Auger matrix elements give clear pictures of top and maximum of p-like local density of states (LDOS) around Si and C in the near-edge VB region. In this talk, a combined use of the Auger and photoemission processes for site-specific information about the local density of states (LDOS) and the leading edge in the VB will be described. Binding energy-corrected Auger line shape for each of Si and C was obtained to identify the valence electronic structure in the particular case of amorphous hydrogenated SiC (a-Si@sub 1-x@C@sub x@:H) thin films fabricated by plasma enhanced chemical vapor deposition. In the C-rich region (x @>=@ 0.6), the leading VB edge was defined by C-2p, while the VB edge was determined by both Si-3p and C-2p in Si-rich region (x < 0.6). The conduction band (CB) edge was assigned by electron energy loss spectroscopy (EELS) with Si-2p electron-associated energy loss. The band gap energies obtained from the VB and CB edges were compared to those from optical absorption measurements.

3:00pm **TF+EL-WeA4 Growth of Oxygen-rich Films on Ru(0001)*, A. Böttcher,*** *B. Krenzer, W. Stenzel, H. Conrad,* Fritz-Haber-Institut, Germany*; H. Niehus,* Humboldt-Universität, Germany

The potential of photoemission electron microscopy (PEEM) has been utilized for monitoring the modifications of Ru(0001) induced by surface oxidation. The PEEM images of the initial oxidation stages exhibit bright patterns appearing on dark background. The former represent the precursor phases of regular oxides, Ru@sub x@O@sub y@. The background reflect the termination of the Ru(0001) surface by the chemisorbed oxygen layer. The growth of the Ru@sub x@O@sub y@ from nucleation centers to a thick oxide film strongly depends on the oxidation temperature. Three phases differing by characteristic morphologies have been distinguished. For low temperatures, TT@sub H@, the Ru@sub x@O@sub y@ phase manifests itself by very bright discs randomly distributed over large dark areas. For moderate temperatures, T@sub H@>T>T@sub L@, long stripes appear and grow along the main crystallographic directions of Ru(0001). This growth is initiated by formation of light grains. Further oxidation proceeds via a growth of star-shaped and linear islands following the hexagonal symmetry of the substrate and leads finally to the formation of an ordered network. The growth modes result from destabilization of the Ru surface.@footnote 1@ The thick oxygen-rich films created under low- and moderate-temperature oxidation regime are thermally unstable. PEEM images become gradually dark when keeping the sample at temperatures higher than the oxidation temperature. This transformation reveals the cluster formation of stoichiometric oxides as well as a rearrangement of Ru and O atoms across the thick oxygen-rich layer. All mesoscopic-scale structures studied offer adsorption sites for surplus atomic oxygen adsorbed when exposing them to oxygen at room temperature. @FootnoteText@ @footnote 1@A. Böttcher, H. Conrad, H. Niehus, J. Chem. Phys. 112 (2000) 4779.

3:20pm **TF+EL-WeA5 In-situ Characterization of Thin Film Growth*, W. Fukarek*,** Research Center Rossendorf, Germany **INVITED**

Real time ellipsometry provides information on the dielectric function and dynamic film thickness when applied to film growth or etching. Density depth profiles can be derived either from refractive index depth profiles or from dynamic growth rate data if the flux of film forming particles is known and the sticking probabilities and sputter yield remain constant during growth. Absolute density depth profiles are obtained by scaling the integral to the areal mass density as obtained from ion beam analysis. In-plane stress in thin amorphous or nanocrystalline films, where diffraction methods can not or only hardly be applied, can be measured in situ also under harsh conditions employing optical sampling of cantilever bending. From real time film thickness and curvature measurement instantaneous stress depth profiles are derived with a depth resolution in the nanometer range. The synergistic effects on the information obtained from ellipsometry, particle flux, and cantilever bending data recorded simultaneously are demonstrated exemplarily for ion beam assisted deposition of boron nitride films. In turbostratic (tBN) films the density is found to increase slightly with film thickness whereas the compressive stress decreases, indicating an increasing quality and/or size of crystallites in the course of film growth. In the case of growth of cubic (cBN) films the density starts to increase rapidly from the value characteristic of tBN up to the density of cBN (3.6 g/cm@super 3@). Comparison with the dark field TEM graph recorded from the cBN reflex reveals that the increase in density coincides with the nucleation and increase in crystallite size of cBN. The density remains constant when coalescence of the cBN crystallites is observed in dark field TEM. In contrast to the growth of tBN the depth profile of the instantaneous compressive stress in cBN films is found to be very complex and not directly related to changes in crystalline structure.

4:00pm **TF+EL-WeA7 Characterization of the Phase Evolution of Boron Nitride Thin Films using Real Time Multichannel Ellipsometry from 1.5 to 6.5 eV*, J.A. Zapien,*** *R. Messier, R.W. Collins,* The Pennsylvania State University

Cubic boron nitride (cBN) is the second hardest material after diamond. This property together with its superior chemical and thermal stability makes it a very promising candidate for hard coating applications. The layered structure of cBN films on crystalline silicon (c-Si) substrates is well documented. It is commonly accepted that a sequence of amorphous and hexagonal (hBN) layers grow prior to cBN nucleation. This sequence has been described by real time measurements including polarized infrared reflectance (PIRR) spectroscopy, and infrared spectroscopic ellipsometry (IRSE). The demand for real time characterization techniques is motivated by the use of complex deposition sequences used to optimize film characteristics. Recently, we have developed a rotating polarizer multichannel ellipsometer with spectral capabilities that extend well into the uv range. With this instrument, 132 spectral points in the ellipsometric parameters (@psi@, @DELTA@) covering the photon energy range from 1.5 to 6.5 eV can be collected with a minimum acquisition time of 24.5 ms, while maintaining sub-monolayer sensitivity. As a result of the uv-extended capabilities, the new multichannel ellipsometer is well suited to study wide band gap materials in real time during preparation. Here we report the use of the uv-extended multichannel ellipsometer to study the growth and layered structure of cBN films deposited on c-Si using two processes: i) rf magnetron sputtering of a BN target with pulsed dc substrate bias, and ii) pulsed dc sputtering of a B@sub 4@C target with rf substrate bias. The phase evolution of the BN films based on the optical response in the visible-uv spectral region has been found to be in good agreement with ex-situ Fourier Transform Infrared Spectroscopy (FTIR) performed at the end of the deposition. The effect of the deposition conditions on the phase evolution and optical properties of the films will be presented.

4:20pm **TF+EL-WeA8 Deposition of Hard Amorphous Hydrogenated Carbon Films from Hyperthermal Hydrocarbon Radicals, Studied by In Situ Real Time Infrared Spectroscopy*, A. von Keudell,*** Max-Planck-Institut für Plasmaphysik, Germany*; K.Y. Letourneur,* TU Eindhoven, Netherlands*; M.C.M. van de Sanden,* TU Eindhoven, Netherlands, The Netherlands

Dense and hard amorphous hydrogenated carbon films are deposited from a cascaded arc discharge from argon and using remote acetylene (C@sub 2@H@sub 2@) injection. The film formation is monitored by means of real time in situ ellipsometry and real time in situ infrared spectroscopy. From an enhanced infrared absorption at 3300 cm@super -1@ at the surface during deposition, corresponding to the stretching mode of sp@super 1@ hybridized CH groups, it is concluded that C@sub 2@H is the dominant growth precursor. This surface enhancement of the concentration of sp@super 1@ hybridized CH groups increases with increasing growth rate and film density. This variation of the growth rate and the variation of the film properties like mass density, hardness and hydrogen content can be well described by the balance between the contribution of C@sub 2@H and C@sub 2@H@sub 2@ to the incorporated carbon flux.

4:40pm **TF+EL-WeA9 In-Situ Monitoring of Adsorption and Film Growth Using Infrared Reflection Absorption Spectroscopy*, V.M. Bermudez,*** *W.J. DeSisto,* Naval Research Laboratory

Chemical methods for thin-film growth and processing, such as CVD, suffer from a lack of techniques for surface-sensitive, chemically-specific diagnostics under steady-state conditions. Infrared reflection absorption spectroscopy (IRRAS) has been demonstrated as a viable approach to addressing this need. Polarization modulation (PM) has been coupled with a Fourier transform IR spectrometer, permitting the use of linear dichroism to distinguish weak, polarized surface absorptions from strong, isotropic gas-phase absorptions. Buried metal layers have been used both to increase the IRRAS sensitivity to adsorbates on nonmetallic surfaces and to impose the high degree of polarization needed for detection of surface species. Numerical modelling, via the Fresnel relations, has also been included as an integral part of the experiment. This approach has been used to observe the different @delta@@sub s@ frequencies of NH@sub 3@ adsorbed on Al nitride, oxide and oxynitride in a 200 Torr NH@sub 3@ ambient, which can be understood in terms of the different Lewis acidities of the surface Al cations. The optical system has been mated with a production CVD facility and used to observe the steady-state growth of Cr@sub 2@O@sub 3@ thin films on Al@sub 2@O@sub 3@ by reaction of Cr(CO)@sub 6@ and O@sub 2@ at @<=@270 °C. The T-dependence of the physisorbed Cr(CO)@sub 6@ coverage measured with PM-IRRAS gives a desorption energy of 11 Kcal/mol, indicating a weak interaction with the substrate. The growth rate of the Cr@sub 2@O@sub 3@ film is first-order in the Cr(CO)@sub 6@ pressure (both quantities having been obtained from IR data). Modeling of the IR data shows interfacial roughness to be important in this system.

5:00pm **TF+EL-WeA10 Investigation of the Subsonic Beam behaviour of an Expanding Thermal Plasma used to Deposit Silicondioxide like Films*, M.F.A.M van Hest,*** Eindhoven University of Technology, The Netherlands, Eindhoven*; D.C. Schram,* Eindhoven University of Technology, The Netherlands, Netherlands*; M.C.M. van de Sanden,* Eindhoven University of Technology, The Netherlands

Silicondioxide like films are deposited using a remote thermal argon plasma generated by means of a cascaded arc (p=0.1 - 0.2 bar). Into this remote argon plasma, which expands into a vacuum vessel (p=0.1 mbar), two precursors are injected. First Oxygen is injected at the arc nozzle, and downstream HMDSO (hexamethyldisiloxane) is injected by means of an injection ring. By studying the behaviour of the expanding beam for various plasma conditions a better insight is created in the plasma chemistry. The plasma is analysed by means or Langmuir probe and Pitot tube measurements. Furthermore the growth is studied in situ by means of HeNe ellipsometry and infrared reflection absorption spectroscopy. By means of the Pitot tube the expanding gas velocity can be measured at various positions in the plasma reactor, and with this the gas flow pattern in the reactor can be determined. First of all the flow pattern is studied for a pure argon plasma. This is done as function of the carrier gas flow (argon) and arc current, but also for different background pressures. Second the flow pattern is studied when the depositing precursors are added to the expanding argon plasma. The Pitot tube measurements show that in the plasma reactor there is a recirculation flow on the outside of the expansion. The Langmuir probe measurements show the ion density in the plasma beam. From the combination of the Langmuir probe measurements and the Pitot tube measurements a possible dissociation mechanism for the deposition precursors will be derived. These results will be combined with the in situ measurements of the film growth to obtain insight in the film growth mechanism.

Vacuum Technology
Room 201 - Session VT-WeA
Vacuum Gas Dynamics

Moderator: J.L. Provo, Sandia National Laboratories

2:00pm **VT-WeA1 A Test Problem for the Holweck Pump*, J.C. Helmer,*** AVS Fellow

The general principles of molecular drag pumping have been understood since since W. Gaede's work in 1913, but it is curious that approximate models have not existed to explain the operation of the Gaede and Holweck molecular pumps over the range of practical application. The laminar flow model for the one-dimensional Gaede pump is now complete. One would infer that the wide channel, Holweck pump model is a two dimensional generalization of the Gaede model. This generalization has not been achieved, although some specific CFD (computational fluid dynamics) solutions have been published.@footnote 1,2@ Our analytic investigation of the Holweck case shows that there is no solution with a parallel flow field, and that compressibility introduces rotation. An approximate solution at high flow rate has been obtained for wide Holweck channels, which illustrates how these issues are resolved. A major difference between the Gaede and Holweck pumps is in the form of the leakage, which is parallel to the channel in the former, and across the channel in the latter. The problem of leakage-limited operation will be discussed. In practical cases the channel depth is small, and the the solution in this dimension is known as a case of Couette-Poiseuille flow. The Holweck geometry may then be idealized in two-dimensions, as a parallelogram lying in a plane with a drag vector of arbitrary direction. @FootnoteText@ @footnote 1@ K. Nanbu & S. Igarashi, "Three-dimensional low-density flows in the spiral grooves of a turbo-molecular pump", Computers Fluids, 21(2), pp221-228, 1992 @footnote 2@ H-P Cheng, R-Y. Jou, F-Z. Chen, Y-W. Chang, "Flow investigation of Siegbahn vacuum pump by CFD methodology", Vacuum 53, pp 227-231, 1999. "Three-dimensional flow analysis of spiral-grooved turbo booster pump in slip and continuum flow", J. Vac. Sci.. Technol. A. 18(2), 543-551, Mar/Apr 2000 .

2:20pm **VT-WeA2 Significance of Bulk Flow Velocity for Turbopump Design*, M.H. Hablanian,*** Varian Inc.*; R. Cerruti,* Varian Inc., Italy

Initially, studies of many aspects of the pumping mechanism of turbomolecular pumps were approached from the high-vacuum side rather than from atmospheric pressure. Therefore, some significant parameters, well known from the discipline of fluid mechanics, have been neglected. One such parameter is bulk fluid stream velocity, which can be a significant engineering consideration for creating an optimized design. Due to the enormous densification ratios achieved in modern turbomolecular pumps, especially of the hybrid or compound variety, the flow velocity at the exit end of the pump is often near zero. This induces a stagnant condition, particularly when backing pumps are very small, allowing, for example, increased back-diffusion of light gases (hydrogen and helium). In addition, the presence of the nearly stagnant gas produces adverse effects on power consumption, which is very significant in newer hybrid turbopumps that can reach 100 mbar exhaust pressure. Attempts to create a single algorithm for a design using one type of impeller do not produce a scheme for a viable pump. The selection of appropriate different types of impellers for the entire pump structure seems to be the best method for optimizing overall performance.

2:40pm **VT-WeA3 A Quantitative Test of Slip-Flow Theory using the Spinning Rotor Gauge*, J.P. Looney,*** National Institute of Standards and Technology*; J. Setina,* Institute of Metals, Slovenia

Although a theory for gas slip flow has been in existence from the time of James Maxwell, no quantitative test of slip flow theory has been undertaken. Typically the slip flow theory of Maxwell is used to extract momentum accommodation coefficients from gas flow data. This is one method for 'measurement' of gas accommodation coefficients. However, this assumes that slip-flow theory is correct and that there is indeed proportionality between the magnitude of the momentum accommodation at the surface and the gas 'slip'. No test of this conjecture has been reported to the author's knowledge. In this talk I will report on the simultaneous and independent measurement of gas momentum accommodation and gas slip coefficients for a group of six spinning chrome steel spheres (spinning rotor gauges) and for four gases (H2, He, N2, and

Ar). The results of these experiments clearly demonstrate the proportionality between the gas slip and momentum accommodation. A detailed comparison of these measurments with slip-flow theory will be made.

3:00pm **VT-WeA4 Power Dissipation in Gaede Stages of Turbomolecular-drag Pumps in Viscous High-pressure Regime***, **R. Cerruti**, S. Giors, J.C. Helmer, A. Netti,* Varian Vacuum Technologies, Italy

Drag Gaede stages are used for extending the operating range of turbomolecular pumps to higher pressures. A practical limit to high pressure operation is set by the power dissipated by these stages, which comes mainly from the friction inside the gas boundary layer. The power has then a direct impact on the rotor temperature and the electrical consumption of the motor. In a previous paper we presented a transitional power consumption model, which allowed to predict the power consumption of a given drag stage up to about 10 mbar, correctly capturing the effect of the transition from molecular to viscous regime, but failing above a critical pressure. @footnote 1@ The present work is aimed to extend the model to higher pressures ranges, where turbulence and other instabilities can not be neglected: above a certain pressure the rotor and stator boundary layers get affected by the centrifugal force field, their structure becomes pressure dependent and eventually turbulent. The simple viscous model is extended in order to incorporate these effects through the definition of an "eddy viscosity", which is a pressure dependent parameter introduced by Prandtl turbulent mixing length theory. The model results, showing the power dissipation growing with pressure in the high pressure regime, are compared with experimental power consumption measurement up to 100 mbar, on single drag stages with different dimensions, different rotational speeds and different gases. The model is aimed to be used in the optimization of the multistage Gaede pumps at very high pressure. @FootnoteText@ @footnote 1@ R. Cerruti, M. Spagnol, J. C. Helmer, "Power dissipation in turbomolecular pumps at high pressure", J. Vac. Sci. Technol. A 17(5), 3096-3102, Sept/Oct 1999.

3:20pm **VT-WeA5 Modelling Micro-Channel Flows with DSMC and a Particle Continuum Method***, **T.J. Bartel**, M.A. Gallis,* Sandia National Laboratories

Advances in micromachining technology have enabled fabrication of MEMS devices. Even at atmospheric pressures, flow through these devices can range from rarefied to transitional due to the length scale and the mean free path. The Direct Simulation Monte Carlo (DSMC) technique, a direct particle based simulation of the Boltzmann equation, is an appropriate and accurate simulation tool for these devices; however, the computational expense of determining subsonic flows is very large. The major issue is one of statistical resolution: the computational particle velocities are at their thermal speeds while the mean gas velocity is at M ~ 0.01. We will present a overview of the issues of using DSMC and show results for micro-channel flows obtained with our massively parallel version. We have developed a new strategy which accelerates convergence to the steady-state. In this method, we have define the computational particle as a mass per time quantity (rho*V*A). Now the computational phase space is not stochastic, but is deterministic based on the resonance time of each computational particle in a cell. This formulation greatly reduces the statistical noise and computational expense experienced in pure particle simulations. We use a Langevin formulation for the viscous and pressure forces. We use the DSMC method to obtain a spatial varying model for the transport properties (similar to a turbulence model) to extend the validity of the continuum method to non-continuum flows. We will compare results from this new method with DSMC and discuss future work. This strategy is more robust and computationally efficient than split domain methods: DSMC is used for a portion of the domain and a continuum solver for the remainder.

3:40pm **VT-WeA6 Flow of Moderately Rarefied Gases Through Short Circular Tubes***, **S.A. Tison**,* Millipore Corporation

The conductance of vacuum geometries is very important for design of vacuum systems. In particular the conductance of cylinders has been exhaustively studied because of its predominant use in vacuum components. While the conductance is well established for these geometries under high rarefied conditions@footnote 1@ the conductance in the transition between rarefied flow and continuum flow is less understood. In particular, phenomena such as the Knudsen minimum identified in long tubes almost a century ago is still an active area for theoretical and experimental study. While long tubes are known to have mimimums in conductance, sometimes less than 20% of the free molecular value, sharp edged orifices do not exhibit this pattern. It is logical to assume that there must exist a relatively short tube which exhibits traits intermediate to long tubes and sharp edged orifices. A series of conductances with length to diameter ratios (L/D) from 100 to 2 have been experimentally studied and compared to transition flow models. Data includes Knudsen numbers from 0.01 to 10 for a variety of noncondensable gases. Results indicate reasonable agreement with models@footnote 2@ and show the disappearance of the Knudsen minimum for short tubes (L/D)=2. @FootnoteText@ @footnote 1@ Clausing, P., Ann. Physik (5) 12, 961 (1932) @footnote 2@ Arkillic, E., and Breuer, K.S., AIAA paper 93-3270, (1993).

4:00pm **VT-WeA7 A Method for Calculation of Gas Flow in the Whole Pressure Regime Through Ducts of Any Length***, **R.G. Livesey**,* BOC Edwards, UK

Useful approaches to the calculation of gas flows in the molecular-continuum transition region have been presented by a number of authors. These have covered particular conditions such as long ducts or orifices with a large pressure difference for example. There is, however, no generally applicable method which enables calculation under all conditions. A particular area of difficulty is the isentropic-molecular transition. The paper presents a simple model which enables calculation for all conditions of long or short ducts and large or small pressure differences. Results are found to agree well with published data.

4:20pm **VT-WeA8 Conic Peak/Dimple Roughness Model for Explaining the Reduction of Flow Rate through Passages with Rough Walls***, **T. Sawada**, W. Sugiyama, M. Yabuki,* Akita University, Japan

Passages with rough walls allow for smaller conductance for rarefied gas flow than passages with smooth walls. For the purpose of clarifying the effects of surface roughness on rarefied gas flow through passages, surface roughness is modeled by circular-conical peaks and dimples with the same base radius. Cones (peaks and dimples) are located in a statistical manner. Cone height and depth are also determined in a statistical manner from the measured angle distributions of actual surface roughness. The following are assumed in the model: (1). Cones are optional in contact with one another. (2). Cones higher than 1.2r(r: radius of base circle) are cut at the height of 1.2r and the upper parts are removed, but the top flat faces are not open for molecules to fly into. (3) The distance traveled by molecules between collisions with cone surfaces on the same macroscopic surface does not affect the macroscopic transfer of molecules. (4) Molecules do not collide with one another during their travel on a macroscopic surface. (5) Molecules are regarded as hard spheres and they scatter on cone surfaces according to cosine law. (6) The height of cone roughness is much smaller than the height of the passage. The calculated results predict well the measured reduction of free molecule and near free molecule flow conductance through channels composed of two flat plates.

4:40pm **VT-WeA9 Free Jets in Vacuum Technologies***, **A.K. Rebrov**,* Institute of Thermophysics, Russia **INVITED**

The knowledge on gas expansion into vacuum or a low density background was of a paramount importance for the development of vacuum technologies throughout their history. The variety of gas sources, of flow parameters in sources and parameters of background gas state sets the problem of jet flows as vast for the analysis. But the classification of flows is possible. The first step is division of gas expansion into vacuum and in a background. The expansion into vacuum can be considered separately for different types of sources (orifices, capillaries, flat slots, Laval nozzles) under different channel Knudsen numbers. The discharge coefficients, the plume of molecular flow, the structure of the free jet, relaxation processes in the jet, the gas mixture issue represent the main interest. By the expansion of gases into a background from some source the structure of jets in the regimes from free molecular to turbulent flow is defined by the source and state of the background gas. The available results of investigations allow to determine the location of different zones and character of flow, including the evaluation of relaxation of the internal energy and condensation effects. New problems of vacuum technologies are in need of determination of the flow parameter distribution with high accuracy. New computational methods can be used for this purpose. The direct simulation Monte Carlo (DSMC) method became a powerful instrument for study of jet flows. It has depreciated attempts to extend the continuum approach on cases of flows with effects of rarefaction. The hybrid DSMC / fluid methods raise the role of computational simulation, taking into account difficulties of experiments. New achievements in theory can provide not only optimization of technology but extraction of physical knowledge by industrial testing as well.

Biomaterial Interfaces
Room 202 - Session BI+NS-ThM

Nanoscale Biology

Moderator: J.J. Hickman, Clemson University

8:20am **BI+NS-ThM1 Engineering Life into Nanofabricated Systems***, **C.D. Montemagno,*** Cornell University **INVITED**

Scientists and engineers have anticipated the potential benefits of integrating engineered devices to living systems at the molecular level for many years. Hybrid systems can potentially possess many of the essential properties of life such as the abilities to "intelligently" self-assemble, repair, and evolve. We will present the results of our efforts to incorporate biological energy transduction processes and cell signaling pathways into engineered nanofabricated devices. In particular, we will illustrate our strategy for fueling, controlling and integrating a F1-ATPase biomolecular motor with a NEMS to create an engineered hybrid device. Included in the presentation will be the initial results of our efforts to develop and demonstrate an integrated F1-ATPase powered NEMS device that is fueled by light-driven ATP production. ATP is synthesized from light using artificial liposomes comprised of reconstituted FoF1-ATP synthase and bacteriorhodopsin. Subsequently, the ATP provides energy to power a recombinant, thermostable F1-ATPase biomolecular motor that is coupled to a NEMS device. We will also present our technique for integrating nanomechanical structures to biomolecular motors with a precision d 40 nm. This work capitalizes on a core feature of living systems: the capability of transforming diverse sources of energy into a generic energy currency that can be universally used. The integration of a synthetic photosynthetic system with NEMS establishes a new mechanism for fueling the next generation of nanoelectromechanical devices. Light is used to produce ATP from ADP and P, the ATP is used by the F1-ATPase biomolecular motor to produce work with ADP and P as waste products. Ultimately, we anticipate that this chemically closed system will be used to pump fluids, open and close microvalves, provide locomotion, generate electricity, and make way for "Smart Dust" applications such as long-lived microscopic intelligence and environmental sensors.

9:00am **BI+NS-ThM3 Powering Molecular Shuttles through an Artificial Photosynthetic System***, V. Vogel, **H. Hess,*** University of Washington*; K. Jardine,* Arizona State University*; J. Clemmens,* University of Washington*; T.A. Moore, A.L. Moore, A. Primak,* Arizona State University*; J. Howard,* University of Washington*; D. Gust,* Arizona State University

The ultimate goal for bioengineers is to be able to engineer systems on a nanoscale as perfect as nature does in cells. Great progress has been made in recent years in biochemistry and biophysics, supplying us with information about the construction principles as well as the details of many cellular subsystems. This information is matched by recent advances in nanotechnology, allowing control of the arrangement of biomolecules on a sub-micron scale. From an engineering point of view the construction of artificial systems, performing different tasks related to the cellular environment, becomes possible. Examples of this approach are the construction of artificial photosystems,@footnote 1,2@ consisting of vesicles doped with antenna molecules, proton pumps and the enzyme ATPase, and the construction of "molecular shuttles",@footnote 3,4@ microtubules moved by motor proteins on a patterned surface. The arising challenge is to combine these subsystems into a larger, more complex system with extended functionality. Here we present a proof-of-principle experiment demonstrating the integration of a transport systems (the "molecular shuttles") with a system providing chemical energy from light (the above mentioned artificial photosystem). In the integrated system we can therefore nonintrusively control the motion of the microtubules through light. The experimental setup consists of a flow cell mounted on an epi-fluorescence optical microscope and illuminated by a laser diode. The surface of the flow cell was patterned with parallel grooves spaced between 30 nm and 1 um apart by shear-deposition of a teflon film@footnote 5@. The motor protein kinesin@footnote 6@ adsorbed preferentially along the grooves providing "tracks" for the motion of the microtubules. The microtubules were fluorescently labeled and bound to the motor proteins in the absence of ATP. The ATP-generating vesicles floated freely in the buffer solution. Illumination of the sample with light absorbed by the vesicles as followed by motion of the microtubules. The motion was mainly directed along the direction of shear of the underlying teflon film. This experiment thus demonstrated that in an integrated system, multiple self-assembled entities cooperate functionally all the way from light harvesting through charge separation across a lipid membrane and ATP-synthesis driven by a proton gradient to ATP-fueled conformational changes of kinesin leading to directed motion of microtubules on uniaxially aligned kinesin tracks. @FootnoteText@ @footnote 1@ Gust, D., T.A. Moore, and A.L. Moore, Mimicking bacterial photosynthesis. Pure & Appl. Chem., 1998. 70(11): p. 2189-2200. @footnote 2@ Steinberg-Yfrach, G., et al., Light-driven production of ATP catalysed by F0F1-ATP synthase in an artificial photosynthetic membrane. Nature, 1998. 392(6675): p. 479-82. @footnote 3@ Dennis, J.R., J. Howard, and V. Vogel, Molecular shuttles: directing the motion of microtubules on nanoscale kinesin tracks. Nanotechnology, 1999: p. 232-236. @footnote 4@ Service, R.F., Borrowing from biology to power the petite: nanotechnology researchers are harvesting molecular motors from cells in hopes of using them to drive nano-scale devices. Science, 1999. 283: p. 27-28. @footnote 5@ Wittmann, J.C. and P. Smith, Highly oriented thin films of poly(tetrafluoroethylene) as a substrate for oriented growth of materials. Nature, 1991. 352: p. 414-417. @footnote 6@ Howard, J., A.J. Hudspeth, and R.D. Vale, Movement of microtubules by single kinesin molecules. Nature, 1989. 342: p. 154-158.

9:20am **BI+NS-ThM4 Unbinding Process of Adsorbed Proteins under External Stress Studied by AFM Force Spectroscopy***, C. Gergely, **J. Voegel,*** INSERM, France*; P. Schaaf,* Institut Charles Sadron (CNRS) Strasbourg, France*; B. Senger,* INSERM, France*; J.K.H. Horber,* EMBL Heidelberg, Germany*; J. Hemmerle,* INSERM, France

We report the study of the unbinding process under a force load f of adsorbed proteins (fibrinogen) on a solid surface (hydrophilic silica) by means of AFM force spectroscopy. By varying the loading rate r, defined by f=r.t, t being the time, we find that, as for specific interactions, the mean rupture force increases with r. This unbinding process is analysed in the framework of the widely used Bell model. Thus typical dissociation rate at zero force entering in the model lies between 0.02 and 0.6 1/s. Each measured rupture is characterized by a force f0 which appears to be quantized in integer multiples of 180-200 pN.

9:40am **BI+NS-ThM5 Single-Molecule Protein-Ligand Bond-Rupture Forces Measured Using the Poisson Atomic Force Method***, Y.-S. Lo, Y.J. Zhu, J.D. McBride, **T.P. Beebe, Jr.,*** University of Utah **INVITED**

It is known that bond strength is a dynamic property that is dependent upon the force loading rate applied during the rupturing of a bond. For biotin-avidin and biotin-streptavidin systems, dynamic force spectra, which are plots of bond strength vs. ln(loading rate), have been acquired in a recent biomembrane force probe (BFP) study [Merkel et al., Nature 397 (1999) 50] at force loading rates in the range of 0.05 to 60,000 pN/s. In the present study, the dynamic force spectrum of the biotin-streptavidin bond strength in solution was extended from loading rates of ~10@super 5@ to ~10@super 9@ pN/s with the atomic force microscope (AFM). The Poisson AFM statistical analysis method was applied to extract the magnitude of individual bond-rupture forces and non-specific long-range interactions from the AFM force-distance curve measurements. In addition, surface characterization methods for the analysis of protein-coated surfaces and AFM tips, both imaging and spectroscopic x-ray photoelectron spectroscopy (XPS) and time-of-flight secondary ion mass spectrometry (TOF-SIMS) will be discussed. The AFM bond strengths were found to scale linearly with the logarithm of the loading rate in two regimes with two different slopes, consistent with the view that multiple energy barriers are present along the unbinding coordinate of the biotin-streptavidin complex. In contrast, the non-specific interactions, which can be separately measured and characterized apart from the specific bond-rupture forces in this method, did not exhibit a measurable dependence on loading rate. The dynamic force spectra acquired here with the AFM combined well with BFP measurements by others, and demonstrated that unbinding forces measured by different techniques are in agreement and can be used together to obtain a dynamic force spectrum covering 11 orders of magnitude in loading rate.

10:40am **BI+NS-ThM8 Measuring the Mechanical Properties of Soft Samples by Atomic Force Microscopy***, **M. Radmacher,*** Universit@um a@t G@um o@ttingen, Germany **INVITED**

The Atomic Force Microscope combines in a very unique way a very high sensitivity in detecting and applying forces (of up to a few 10's of piconewton), a high accuracy in positioning a sharp tip relativ to the sample in all three dimensions (of up to a few Angstrom), and the possibility to be operated under physiological conditions. This combination allows experiments not possible before, particularly in the field of biophysics and soft materials. One example is the mapping of mechanical properties with high spatial resolution of polymeric films and living cells. In living cells it is possible to probe the mechanics during dynamic processes like cell migration and cell division.

11:20am **BI+NS-ThM10 Protein Adsorption and Monocyte Activation on Ge Nanopyramids*, B. M@um u@ller,*** ETH Z@um u@rich, Switzerland*; M. Riedel,* ProBioGen, Germany*; R. Hofer, E. Wintermantel,* ETH Z@um u@rich, Switzerland

The performance of an implant material depends crucially on its surface architecture or morphology. The significance of topographic features with micrometer size on cell shape and function has been clearly demonstrated. The power of features on the nanometer scale is still under discussion. In order to get an insight into the responds of monocytes onto a well-defined substrate nanostructure, we have grown germanium nanopyramids on Si(100) in a natural way by epitaxial growth, i.e. without any lithographic technique. The density of the pyramids (hut and dome cluster) is adjusted varying the substrate temperature during deposition. The morphology of the oxidized pyramids is quantified by ex situ atomic force microscopy. To characterize the nanostructure roughness further, contact angles of water under dynamic conditions are measured in comparison with the bare Si wafer and flat Ge films on Si. The receding angles show a significant increase with pyramid density. The amount of the selected proteins g-globulin and albumin adsorbed on the nanostructures is determined spectroscopically with labeled proteins. It raises with pyramid density. The impact of nanostructuring on the biological activity of adsorbed g-globulin is addressed by immunosorption with an anti-g-globulin antibody. These data reveal that the amount of active g-globulin does not scale with the adsorbed one. Nanoscale roughness even decreases the activity. The in vitro assays with monocytes that allow studying specific aspects of inflammatory reactions of the body - an important aspect of the biocompatibility, are based on the monocyte-like cell line U937. After 5 days in vitro, the cell performance is characterized microscopically and by the secreted cytokines IL-1b, IL-1ra and TNF-a. For the CVD grown samples, a roughness increase leads to reduced cytokine expression. Consequently, implants with nanoscale roughness gives rise to less inflammatory reactions.

Dielectrics
Room 312 - Session DI+EL+MS-ThM
Ultrathin Dielectrics and Interfaces

Moderator: Y.J. Chabal, Bell Laboratories, Lucent Technologies

8:20am **DI+EL+MS-ThM1 Oxidation of Clean and H-passivated Silicon by Molecular and Atomic Oxygen*, X. Zhang,*** Rutgers University*; Y.J. Chabal,* Bell Laboratories, Lucent Technologies*; E. Garfunkel,* Rutgers University*; S.B. Christman, E.E. Chaban,* Bell Laboratories, Lucent Technologies

The need for uniform and ultra-thin silicon oxides in microelectronics requires a fundamental understanding of the initial oxidation of both clean and H-passivated (HF-etched) silicon in oxygen. We have undertaken a systematic infrared absorption study of molecular O@sub 2@ and atomic O oxidation of H-passivated flat and vicinal Si(111) and Si(100) surfaces. Using an IR transmission geometry for full access to Si-O stretch (900-1250 cm@super -1@) and Si-H bending (600-850 cm@super -1@) modes, we can directly observe the incorporation of oxygen even after H-desorption under ultra-high vacuum conditions. Furthermore, hydrogen at steps can be spectrally distinguished from H on terraces, thus making it possible to correlate the kinetics of H elimination with oxide formation as a function of surface structure. We find that upon 1 Torr exposure at 300@super o@C, the bonding of step hydrogen is preferentially altered on the H/Si(111) surface, with dihydride steps being the most reactive. Yet, the rate of oxidation does not scale with the step density, indicating that direct oxidation of terraces takes place simultaneously. For the Si(100) surface, we contrast the oxidation of the HF-etched (atomically rough surface) with that of the smooth H-Si(100)-(2x1) surface prepared in HHV and that of the clean Si(100)- (2x1) surface in order to extract the mechanism for molecular O@sub 2@ dissociation.

8:40am **DI+EL+MS-ThM2 New Oxidation Process Using Collimated Hyperthermal Ozone Beam*, T. Nishiguchi,*** *Y. Morikawa, M. Miyamoto,* Meidensha Corporation, Japan*; H. Nonaka, A. Kurokawa, S. Ichimura,* Electrotechnical Laboratory, Japan

As the electronic devices are scaled down, using more reactive process gas than molecular oxygen is required to fabricate an ultra-thin highly reliable Si dioxide film for the gate oxide in MOSFET. We used ozone as an oxidant gas and achieved the enhanced initial oxidation rate, resulting in lower temperature oxidation process. In our experiments using highly concentrated ozone gas, more than 3nm Si dioxide film was obtained within 30 minutes under the conditions of 873K of Si temperature and 10Pa of ozone pressure, where the oxidation hardly proceeds by molecular oxygen. In the present study, we carried out the laser ablation of solid ozone in order to obtain collimated ozone beam on the purpose of applying ozone beam to new oxidation processes such as local oxidation of patterned Si surface (e.g. oxidation of a bottom part of a trench). We irradiated a KrF pulsed excimer laser light to highly concentrated solidified ozone that was adsorbed on the sapphire plate cooled down to 30-60K by cryocooler in an UHV chamber. We could obtain collimated ozone beam (within 20° spread) whose supply (typically 10@super 16@ molecules per laser pulse), concentration (typically 70%) and translational energy (3eV maximum) were controlled through the laser ablation conditions such as the laser fluence. Not only the local oxidation but also even lower temperature process is expected using this high-translational-energy (hyperthermal) ozone beam. We will demonstrate the initial oxidation profile for the first 1000 laser shots by Auger Electron Spectroscopy and discuss the applicability of this ozone beam to the semiconductor process.

9:00am **DI+EL+MS-ThM3 Nondestructive Investigation of the Si/SiO2 Interface by Spectroscopic Ellipsometry, Reflectance Difference Spectroscopy, Second Harmonic Generation, and X-ray Photoelectron Spectroscopy*, J.F.T. Wang,*** *J.W. Keister, Y.M. Lee, G. Lucovsky, J.E. Rowe, D.E. Aspnes,* North Carolina State University

We report results of a systematic study with various nondestructive techniques of buried interfaces between Si and thin gate oxides thermally grown at 700C and rapid-thermal-annealed at temperatures to 900C. The objectives are to understand the optical properties, the step structure, and the nature of the chemical bonding of the interface and to determine the limits to which the various nondestructive probes, alone and in combination, can provide this information. We examine in particular data obtained as a function of heat treatment and surface orientation (miscuts 2, 4, 8, 10 degrees off (001) toward the nearest (111); (113); (111); and (110)), with emphasis on the vicinal (001) orientations. The RD spectra of all as-oxidized vicinal (001) samples decrease by nearly a factor of 5 for the 900C RTA, indicating step-density reduction and a net smoothing of the interface. Except for the 2 deg sample, which shows basically no signal, these spectra become essentially identical to the spectra of chemically etched, H-terminated vicinal (001) surfaces. All such spectra have the appearance of RD lineshapes obtained on (113) surfaces, which are nominally dominated by double-height steps. The ellipsometric data differ mainly in overlayer thickness, but interface information can be extracted through least-squares analysis assuming interface spectra of Si in amorphous and +1 and +2 charge states. To assist in this analysis we orthogonalize the fitting parameters to determine which combinations are best determined by the data. The results indicate that the best reference data are those obtained on H-terminated (111) surfaces. The interface XPS spectra become much more consistent after rapid thermal annealing, with the (001) and (111) spectra being dominated by Si in +2 and +1 charge states, respectively, as expected. This provides further evidence of a reduction in roughness with annealing.

9:20am **DI+EL+MS-ThM4 Core-level Photoemission of Interface States on SiO@sub 2@/Si: Substrate Orientation Effects*, J.E. Rowe,*** Army Research Office*; J.W. Keister, J.F.T. Wang,* North Carolina State University*; G.J. Jackson, T.E. Madey,* Rutgers University*; D.E. Aspnes,* North Carolina State University

High resolution soft X-ray photoelectron spectroscopy (SXPS) with synchrotron radiation is used to study the interface of mis-cut SiO@sub 2@/Si(100) [i.e. stepped interface] of device quality ultrathin gate oxides. Our studies were performed on thin oxides grown by thermal oxidation in pure O@sub 2@ at a temperature of 600@degree@C and pressure of ~760 Torr. Our data can be well described by five different Si species due to Si in different oxidation states which are usually labeled Si@super 0@, Si@super +1@, Si@super +2@, Si@super +3@, and Si@super +4@. We have studied a number of samples prepared as described above and find that the energies relative to the Si0 peak are 0.95 eV, 1.80 eV, 2.50 eV, and 4.00 eV for the Si@super +1@, Si@super +2@, Si@super +3@, and Si@super +4@ peaks respectively. For this study, we define the transition region as the region containing Si in intermediate oxidation states (Si@super +1@, Si@super +2@, Si@super +3@). We find a transition-region Si suboxide concentration of 1.3 x 10@super 15@ cm@super -2@ assuming an escape depth of ~7 @Ao@ at a photon energy of 200 eV for samples annealed after growth at temperatures of ~900 @degree@C . This transition region is that in excess of the density ~1 monolayer of Si@super

+1@ expected for the most abrupt SiO@sub 2@/Si(111) interface in terms of the Si(111) layer density of 7.8 x 10@super 14@ cm@super -2@. The I@sub 1@ interface peak is largest for (111) and decreases substantially for (113), (110), and for stepped (100) substrates. The total interface density appears to be lowest for Si(100) with a modest step density introduced by a 2@degree@ mis-cut. The step-dependent behavior is consistent with that reported using second harmonic generation. The total concentration of suboxide derived from SXPS data is dependent on the uniformity of SiO@sub 2@ films as well as data modeling, i.e., fitting of the data; both will be discussed.

9:40am **DI+EL+MS-ThM5 Spectroscopic and Electrical Characterization of the Evolution of Chemical Oxides Into Ultrathin Gate Oxides***, **J. Eng, Jr.,** R.L. Opila, J.M. Rosamilia, J. Sapjeta, Y.J. Chabal, B.E. Weir, P. Silverman, T. Boone, R.L. Masaitis, T. Sorsch, M.L. Green,* Bell Labs, Lucent Technologies

The goal of this study is to understand how the structure of wet chemical oxides change during oxidation, and to determine whether the quality of ultrathin oxides is sensitive to the type of of wet chemical treatments. Four wet chemical treatments were examined: 1. standard RCA, with an SC1 step (ammonium hydroxide and peroxide) followed by an SC2 step (hydrochloric acid and peroxide), 2. modified RCA, with an HF etch between the SC1 and SC2, 3. ozonated water, and 4. HF. X-ray photoelectron spectroscopy (XPS) and infrared spectroscopy (IR) have been used to probe the structure and composition of the wet chemical oxides. IR probes the long range order in the films, while XPS probes the local Si stoichiometry. Both techniques show that the ozone oxide has the highest quality. Despite large differences in the initial quality of the wet chemical oxides, rapid thermal oxidation of the chemical oxides produces oxide films that are spectroscopically similar. Electrical properties of the oxides will correlated with the spectroscopic studies.

10:00am **DI+EL+MS-ThM6 Studies on Accurate Determination of the Physical Thickness of nm Gate Oxides and its Correlation with the Electric Thickness***, **D.W. Moon**, H.K. Kim, H.J. Lee, H.M. Jo,* Korea Research Institute of Standards and Science, Korea*; H.S. Jang, H. Hwang,* Kwangju Institute of Science and Technology, Korea

Accurate Determination of nm gate oxides is critical for the development of nanoelectronic devices as well as for CMOS device scaling beyond 100 nm. In semiconductor industries, the thickness of gate oxides has been measured by ellipsometry. However, the accuracy has been not evaluated especially for gate oxides thinner than 10 nm. Recently, TEM and spectrometric ellipsometry(SE) have been used to measure the physical thickness of nm gate oxides and the electric methods such as I-V an C-V have been modified to include quantum effects. In this work, to estimate the uncertainty and improve the accuracy of the methods used for gate oxides thickness determination, TEM, SE and Medium Energy Ion Scattering Spectroscopy(MEIS) were used to determined the physical thickness of 6 gate oxides from 9 nm thick to 1.5 nm native oxide thick. MEIS can analyze the composition and structure of ultrathin films with atomic layer depth resolution. It was investigated that MEIS can be a reference for gate oxide thickness determination down to 1-2 nm. The difference of the physical thickness determined with TEM, SE and MEIS were discussed and compared with the electric thickness determined by I-V and C-V methods. For the gate oxides studied, the thickness determined by the Si MEIS peak was 1.5 nm thicker than that by the O MEIS peak. The thickness determined by SE and TEM was between the two values, while SE gave ~0.5 nm higher thickness than TEM. However, with the interlayer thickness, TEM thickness approached that of Si MEIS peak thickness. The electric thickness determined with I-V and C-V was close to that of Si MEIS peak thickness within 0.2nm. The thickness by SE is quite sensitive to the refractive index value used for fitting, especially for gate oxides thinner than 5nm. Based on this multi-disciplinary approach, it will be discussed how to provide standards for nm gate oxides approaching the limit of CMOS and how to transfer the standards to SE which is widely used in semiconductor process lines.

10:20am **DI+EL+MS-ThM7 Bonding of Nitrogen in Silicon Oxynitride Films***, **R.L. Opila**, J. Eng, Jr., Y.J. Chabal, K.T. Queeney,* Bell Laboratories, Lucent Technologies*; J.P. Chang,* University of California, Los Angeles

Silicon oxynitride is a promising candidate to replace silicon dioxide in the next generation of microelectronic devices, but key aspects of the nitrogen chemistry in this material remain unresolved. This talk describes a twofold approach for understanding nitrogen bonding in these materials. The first approach employs surface analytical techniques, including photoelectron spectroscopy, infrared spectroscopy and near edge x-ray absorption fine structure, to study how oynitride precursors, suchas as nitric acid, nitromethane, and ammonia, react with silicon surfaces. The second approach uses the previous analytical techniques, along with electron spin resonance spectroscopy, to compare the nitrogen bonding states in silicon oxynitride and silicon nitride films prepared by thermal growth and ion implantation. Significant differences in the distribution of nitrogen bonding states and point defects are observed and correlated with the method of film preparation.

10:40am **DI+EL+MS-ThM8 Photoemission Investigation of Nitrogen Incorporation at the Si/SiO@sub 2@ Interface***, J.E. Rowe,* Army Research Office*; **J.W. Keister,*** North Carolina State University

Monolayer incorporation of nitrogen at the Si/SiO@sub 2@ interface enhances the reliability and electrical characteristics of this nearly perfect interface for ultrathin SiO2 layers.@footnote 1@ In this paper we demonstrate that the Si(100)/SiO@sub 2@ interface is chemically sensitive to the nitrogen concentration. The nitrogen (1s) Soft X-ray Photoemission Spectroscopy (SXPS) peak was measured for varying degrees of N incorporation using the Advanced Light Source synchrotron at LBL National Lab. The broad width of the N(1s) SXPS peak lineshape is consistent with a large degree of final-state, Gaussian phonon broadening, and is comparable to O(1s) line. However, unlike the O(1s) line which is not especially chemically sensitive, the N(1s) line shows a clearly measureable, interface peak shift@footnote 2@ with increasing N incorporation. The average interface peak binding energy is ~0.75 eV greater than that recently reported for thick "bulk" films of Si3N4 with Al-K" XPS. To a lesser degree, the peak shape is seen to change as well. In particular, the peak width minimizes near to the value ~1.0 ML N incorporation, which is also the level at which devices interfaces perform best electrically. @FootnoteText@ @footnote 1@ G. Lucovsky, A. Banerjee, B. Hinds, B. Claflin, K. Koh, H. Yang. J. Vac. Sci Technol. B 15(4) 1074-1079 (1997). @footnote 2@ J. W. Keister, J. E. Rowe, J. J. Kolodziej, H. Niimi, H.-S. Tao, T. E. Madey, G. Lucovsky. J. Vac. Sci Technol. A 17(4) 1250-1257 (1999).

11:00am **DI+EL+MS-ThM9 Investigation of Fluorine in Dry Ultrathin Silicon Oxides***, **G. Vereecke**, E. Röhr, R.J. Carter, T. Conard, H. Dewitte, M.M. Heyns,* IMEC, Belgium

As critical dimensions of integrated circuits continue to decrease, insulators with dielectric constants higher than silicon dioxide will be introduced in capacitors and transistors. However an ultrathin (< 1 nm) silicon oxide layer will generally be needed at the interface between Si and high-k layers. In cluster tools integrating surface preparation and dielectric deposition, vapor HF chemistries are envisaged to etch the native oxide prior to oxide growth. This HF etch leaves F on the surface of the Si wafer, which gets incorporated into the growing oxide. In addition, the silicon subsurface has also been proposed as a source of the F found in these oxides. The presence of F may be beneficial or detrimental for the properties of these layers depending on application, F location, and layer thickness. We have evaluated the sources of F in ultrathin oxides grown by UV/O2 at room temperature in an experimental vapor phase cleaning tool. Surface pretreatment was either by in-situ HF/methanol vapor process or by ex-situ wet HF dip followed by a DIW rinse. Evidence was found for F cross-contamination from the tool gaspanel when the HF etch step was performed in-situ. After correcting for this, F atomic concentrations in oxides grown on vapour HF and wet HF treated surfaces were of about 5 % and 2 %, respectively. The former would lower the dielectric constant of the layer if homogeneously distributed. The level of F contributed by the subsurface was estimated with oxides grown on wet HF treated surfaces in a specially built quartz chamber with no F contamination. No F was detected in these oxides, which indicates that the level of subsurface F is lower than previously reported. Ultrathin oxides continued to grow when exposed to air. This raises concern about their stability during the deposition and annealing of high-k layers. XPS results suggest that this is related to the exchange of labile F groups in the films.

11:20am **DI+EL+MS-ThM10 Studies on Electrical Properties of Ultrathin Oxides of Silicon Grown by Wet Oxidation at Low Water Vapor Pressure***, **V.K. Bhat**, K.N. Bhat, A. Subrahmanyam,* Indian Institute of Technology, India

The rapid downscaling of the device dimension has increased the interest in the ultrathin (< 5 nm) oxides of silicon. Ultrathin oxides with thickness uniformity and good electrical properties are required for the silicon submicron devices. In general, the dry oxidation is being followed to grow these ultarthin oxides. Wet oxidation is not considered for the growth of ultrathin oxides of silicon because of the following reasons: i) high growth rate associated with the conventional wet oxidation at 1 atm. water vapor pressure and ii) large density of electron trapping centres present in the wet oxide. In the present study we report the results on the electrical properties of ultrathin oxides of silicon grown by wet oxidation at low (0.04 atm.) water vapor pressure. Ultrathin oxide of silicon is grown at 900°C on n-type single crystal silicon, single side polished, (100) oriented and having 1-10 @ohm@ cm resistivity (procured from M/s Wacker GmbH, Germany). The grown ultrathin oxides are characterized for their electrical properties by fabricating MOS tunnel diodes (aluminum is thermally evaported with a metal mask on to the ultrathin oxide). The capacitance-voltage (C-V), conductance-voltage (G-V) and current-voltage (I-V) charcteristics of the MOS tunnel diodes are studied. The interafce state density (D@sub it@) and the density of the fixed oxide charge (Q@sub f@) are being calculated. The grown ultrathin oxide thickness is estimated from the measured C-V characteristics and are in the range 2.5-5.0 nm. The oxide growth rate is found to be linear. The charge trapping characteristics of the ultrathin oxides are studied by using consatnt current stress (CCS) technique. The decrease in the gate voltage is observed with the stress time. This observation may be attributed to the positive charge trapping in the oxide during the CCS. The charge trapping is found to be oxide thickness dependent and it decreases with the decrase in the oxide thickness.

11:40am **DI+EL+MS-ThM11 Properties of SiO@sub 2@ Thin Films Deposited at Low Temperature on SiGe and Si Samples in O@sub 2@/TEOS Helicon Plasmas***, **A. Goullet**, D. Goghero, V. Fernandez, A. Granier,* Institut des Matériaux Jean Rouxel, France*; F. Meyer,* Université de Paris XI, France*; G. Turban,* Institut des Matériaux Jean Rouxel, France

Silicon dioxide thin films are deposited at low pressure (< 5mTorr) and temperature (<200° C) on Si@sub 1-x@Ge@sub x@ epi-layers and silicon substrates in oxygen rich O@sub 2@/TEOS helicon plasmas. The growth of SiO@sub 2@ films and the evolution of the interfacial layer under applied radio frequency bias voltage (0, -100, -200 V) are investigated using a UV-Visible phase modulated ellipsometer (1.5-5 eV). The structural properties of the films are studied using infrared transmission spectroscopy, wet chemical etching and spectroscopic ellipsometry. Very thin (<10 nm) SiO@sub 2@ films deposited in the same conditions are investigated by X-ray photoelectron spectroscopy and spectroscopic ellipsometry to gain better insight of the oxide/semiconductor interface. The ion energy is found to be a significant parameter both for film properties and deposition rate. Use of radio frequency bias is effective in producing high quality SiO@sub 2@ films but an amorphized transition layer is detected in this case as evidenced by ellipsometric data modeling. The increase in the ion energy is also responsible for the presence of an additional oxidation state which appears on the Ge 3d XPS peak. Complementary capacitive C(V) measurements of grown oxides have been performed using metal-oxide-semiconductor samples. An increase in the fixed oxide charge and interface state densities as a function of the applied bias voltage is observed for silicon substrates whereas the electrical properties of the films deposited on Si@sub 1-x@Ge@sub x@ are rather insensitive to the deposition conditions.

Material Characterization
Room 207 - Session MC-ThM

Polymer Characterization

Moderator: B.C. Beard, Akzo Nobel Chemicals

8:20am **MC-ThM1 Quantification of Polymer Surface Composition Based on ToF-SIMS Data***, **P. Bertrand**,* Université Catholique de Louvain, Belgium **INVITED**

Time-of-Flight Secondary Ion Mass Spectrometry is nowadays intensively used for polymer surface characterization. The fingerprint nature of ToF-SIMS spectra acquired in static conditions is now well established. Characteristic molecular fragment ions can be used for identification of polymer and organic materials present at the surface. The aim of this presentation is to discuss some issues related to surface quantification with this technique. This is of special importance for applications where copolymers and polymer blends are involved. First, we will discuss the use of end group ToF-SIMS signals. Our recent results obtained on monodisperse polystyrene samples show that ToF-SIMS is very sensitive to end groups. Their intensity can be used, after appropriate calibration, to quantify molecular weight at the surface. Some end groups (sec-butyl) are seen to influence also the intensity of main chain fragments. This is due to a specific interaction with the first neighboring repeat unit. It consists in a mechanism of H transfer, with no long-range (intermolecular) influence. So, the end group signals allowed us to quantify the surface composition of polystyrene blends with close molecular weights but different end groups. Second, we will discuss the use of characteristic fragment intensity and intensity ratios for blend and copolymer surface quantification. For polystryrene / poly (2,6-dimethyl-1,4-phenylene oxide) blends, which are miscible and do not exhibit any surface segregation, the intensity of the characteristic ions is seen proportional to homopolymer bulk concentration, allowing a staighforward surface quantification. But for random copolymers, different situations are observed. For random styrene butadiene rubbers, an appropriate choice of ions leads to "bulk like" surface composition, as expected. However, styrene / methyl methacrylate random copolymers, exhibit strong matrix effects due to a specific interaction between adjacent species taking place during the secondary ion emission. This outlines the need of understanding the fragmentation pathways in order to use ToF-SIMS intensities for surface quantification. Another approach would be the use of "full spectrum" chemometrics multivariate methods.

9:00am **MC-ThM3 Characterisation of Polymer Additives by Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS)***, **R. Kersting**, B. Hagenhoff,* TASCON GmbH, Germany*; D. Rading, E. Niehuis,* ION-TOF GmbH, Germany

In continuation of our ongoing studies concerning the characterisation of polymer additives in their respective host polymers we have concentrated on the investigation of the influence of the primary ion parameters on the emission behaviour of characteristic additive ions. The additives, mostly antioxidants, were incorporated into low densitiy polyethylene (LDPE) or spin coated onto virgin LDPE in concentrations between approx. 500 and 2000 ppm. Thus ion emission from thick polymer materials could be studied. Reference samples without the polymer host were prepared by spin coating the additives onto bare Si wafers. Both, monoatomic (Ga@super +@, Au@super +@) and polyatomic (SF@sub 5@@super +@, Au@sub 2@@super +@) ions were used for sample excitation. Additionally, the energy of the respective primary ions was varied between 1 and 10 keV. The talk will describe the influence of the respective primary ion parameter onto yield and efficiency of the desorbed secondary ions. The consequences for the quantification of polymer additives in "real world" samples will also be discussed.

9:20am **MC-ThM4 Surface Composition of Poly(imidesiloxane) Copolymers Containing Multiple Siloxane Lengths***, **C.M. Mahoney**,* State University of New York at Buffalo*; J Rosenfeld, S.R. Rojstaczer,* Occidental Chemical Corporation*; J.A. Gardella,* State University of New York at Buffalo

Polyimidesiloxane copolymers (SIM) are becoming increasingly important materials for microelectronic applications due to their excellent adhesive properties, low dielectric constants and good overall thermal and mechanical properties. Hence it is of importance to study the surface and interfacial properties of this polymer system. More recently it has been shown through depth profiling using Electron Spectroscopy for Chemical Analysis (ESCA) that an increase in the siloxane chain length will result in an increase in the thickness of the siloxane layer at the surface.@footnote 1@ The effect of incorporating two or more different siloxane segment lengths into the same copolymer system, on the surface properties, has not been investigated. It is of importance to determine whether or not there is preferential segregation of certain segment lengths over others in SIM copolymers containing multiple siloxane lengths. A series of poly(imidesiloxane) (SIM) copolymers, based on a,w'-aminopropylpoly(dimethylsiloxane) (PDMS) of varying molecular weights, 2,2-bis(4-[4-aminophenoxyl]phenyl)propane (BAPP), and 4,4'-oxydiphthalic anhydride (ODPA) was synthesized in our laboratories. In this series, the total composition of PDMS was maintained at 10%, while the segment length composition of the PDMS was varied (e.g. 5% Mw = 252g/mol, 5% Mw = 832.5g/mol vs. 1% Mw = 252g/mol, 9% Mw = 832.5g/mol). This polymer series was analyzed using ESCA and Time of Flight Secondary Ion Mass Spectroscopy (ToF-SIMS). Angle-dependent ESCA results suggest that there is preferential segregation of the longer PDMS segment lengths to the surface. ToF-SIMS can be used to further confirm the occurance of this preferential segregation. The peel strength of the polymer series to a standard Ni/Fe alloy 42 was measured , and the results correlate well with the ESCA and ToF-SIMS data. @FootnoteText@ @footnote 1@ Zhao, J; Rojstaczer, S.R.; Chen, J.; Xu, M.; Gardella, J.A. Macromolecules. 1999, 32(2), 455.

9:40am **MC-ThM5 High Spatial Resolution XPS and FTIR: An Approach to 3-D Characterization of Polymer Blends***, **K. Artyushkova**, G. Czwerniec, J.E. Fulghum,* Kent State University*; B. Wall, J. Koenig,* Case Western Reserve University

Correlative XPS and FTIR studies of the complex structure of PVC/PMMA polymer blends will be presented. The comparable lateral resolution and real-time imaging capabilities of both techniques allow for a direct comparison of surface (XPS) and bulk (FTIR) measurements of polymer blends. In order to eliminate substrate influence and film-to-film variations, the same areas on the polymer films were analyzed by both methods. The effect of PMMA molecular weight on surface separation and segregation was evaluated using six blends with a constant PVC molecular weight and a PMMA molecular weight varying from 75 kDa to 2,132 kDa. The imaging capabilities of both techniques were used for a qualitative comparison of the heterogeneous structure of the blends, while a quantitative comparison of bulk and surface compositions utilized small area spectroscopy from XPS and FTIR. Based on the quantitative analysis, we can conclude that surface segregation of PMMA increases with increasing molecular weight. Comparison of Attenuated Total Reflectance (ATR) FTIR, bulk FTIR and large area XPS analyses provides adiditional information about component distrubution in the blend. The combination of high-spatial resolution XPS and FTIR provides a more complete method for characterizing complex polymer films containing differing surface and bulk compositions. This work has been partially supported by NSF ALCOM (DMR89-20147)and 3M. The XPS was funded by a grant from the Keck Foundation and by NSF CHE-9613880.

10:00am **MC-ThM6 Iron Metallization of Fluorinated Organic Films; A Combined XPS and AFM Study***, **S.R. Carlo**, A.J. Wagner, D.H. Fairbrother,* Johns Hopkins University

The evolution of the metal-organic interface during iron mediated metallization of fluorinated organic surfaces has been studied using X-ray Photoelectron Spectroscopy (XPS) and Atomic Force Microscopy (AFM). Poly(tetrafluoroethylene) (PTFE) and a semi-fluorinated self-assembled monolayer (CF@sub3@(CF@sub2@)@sub7@(CH@sub2@)@sub2@SH, CF-SAMs) formed on Au were used as substrates. Reaction of Fe resulted in defluorination of each film, production of a carbonaceous overlayer and exclusive formation of iron (II) fluoride. A metallic iron overlayer was formed concurrently with FeF2 during deposition on CF-SAMs and following extended iron exposures with PTFE substrates. X-ray treatment of metallized PTFE caused an increase of the FeF@sub2@ content in the metal-organic region. Ex-situ AFM measurements revealed that the frictional characteristics of the surface increase during the initial stages of metallization associated with defluorination and FeF@sub2@ formation. At higher Fe exposures the surface friction decreased as a metallic overlayer evolved. Results of metallization using other metals will also be presented.

10:20am **MC-ThM7 Interactions of Cu(I) with the Surface of a Novel Poly(imidazole)***, **A.L. Marsh**, D.J. Burnett,* University of Michigan*; D.A. Fischer,* National Institute of Standards and Technology*; P.G. Rasmussen, J.L. Gland,* University of Michigan

The surface of a novel poly(imidazole), polyvinazene, was characterized using both X-ray Photoelectron Spectroscopy (XPS) and Near Edge X-ray Absorption Fine Structure (NEXAFS) at both the C-K-edge and N-K-edge. Polyvinazene, which is based on the monomer 2-vinyl-4,5-dicyanoimidazole, is a novel polymer which has a high temperature stability and can be easily processed from solutions in concentrated aqueous ammonia into thin, yellow films. XPS was used to determine the chemical composition of the polyvinazene surface, while NEXAFS was used to determine the structure of the polymer surface before and after copper doping. Since NEXAFS probes unfilled molecular orbitals, it is capable of distinguishing between the specific bonds present in the polymer, so the bonding sites for Cu(I) can be determined. In addition, the orientation of the imidazole ring has been determined since resonance intensities for NEXAFS obey electric dipole selection rules. Based on NEXAFS experiments, Cu(I) interacts favorably with the amide N on the imidazole ring. Also, the imidazole ring is oriented close to the surface and away from the surface normal, which supports the claim that the polymer chains are linked together through hydrogen bonds. Determination of the bonding site of Cu(I) to the polymer and the structure of the polymer surface hopes to aid in design for materials such as sensors, catalysts, and metallized polymer films.

10:40am **MC-ThM8 Study of Semicrystalline Poly(ethylene terephthalate) by Atomic Force Microscopy***, M. Kovar, U. Gorodzinsky, **P.R. Norton**,* University of Western Ontario, Canada

We studied the surface topography of isothermally crystallized polyethylene terephthalate (PET) films by atomic force microscopy (AFM). Annealing a flat amorphous PET film at 150 @super o@C produces a semi-crystalline film which is rough on several length scales. We found good correlation of the height (3.5 nm) of small topographical features with the lamellar thickness determined by small angle X-ray scattering in previous studies. It was shown that larger agglomerates (large peaks) are multiples of small ones. The phenomenon is known as lamellar stacking. We hypothesize that the surface corrugation originates as follows: elevated (more crystalline) areas are created at the locations of crystallization nuclei. The polymer chains fold to create lamellar structures and pull "loose" ends out of amorphous regions. Subsequently, lamellar stacks grow using a similar mechanism forming the elevated regions and leaving recessed (less crystalline) ones behind Surprisingly, the density of the small topographical features is the same in the recessed and elevated regions, apparently indicating similar crystallinity, while interfacial force microscopy (IFM) data [J. Mater. Res. 12 (1998) 3565] show the elevated regions to be more crystalline. This apparent conflict results from the sensitivity of AFM phase imaging to only the outermost surface of the film compared to IFM, even for IFM indentation depths of a few nm. Therefore, the variations in the density of crystalline domains (lamellae) that are visible in AFM phase images represent a surface phenomenon that cannot be simply correlated with the state of sub-surface regions.

11:00am **MC-ThM9 Morphology of Catalytically Formed Polyethylene on a Planar Model System for the Phillips (CrOx / SiO2) Catalyst***, P.C. Thuene, J. Loos, P.J. Lemstra,* Eindhoven University of Technology, The Netherlands*; **J.W. Niemantsverdriet**,* Eindhoven University of Technology, The Netherlands, Netherlands

One of the neglected topics of polymerization catalysis is the so called nascent morphology of polyolefins which is the result of polymer formation below the melting temperature and simultaneous crystallization. Nascent polyolefins have special physical properties, which might be controlled and manipulated to enhance the processability of certain high performance polyolefins. Using a planar model system for the chromium on silica catalyst for ethylene polymerization we have obtained AFM images of polyethylene in the state of nascent morphology. By diluting the number of catalytically active sites on the model, individual islands of polymer, produced by single sites have been observed.

11:20am **MC-ThM10 Nano-Mechanics of Polymer Surfaces***, C. Steffan, H. Liu, **R.M. Winter**,* South Dakota School of Mines and Technology

We report on the nano-mechanical properties (elastic modulus and time dependent phenomena) of polymer surfaces as they relate to polymer matrix composites. This work is prompted by the desire to engineer macroscopic polymer matrix composite properties by systematic variation of nano- and micro-scopic properties of the interphase. The interfacial force microscope, a scanning probe microscope, which utilizes a non-compliant force sensor is employed to characterize the surfaces. Force-displacement curves are obtained, from which, elastic modulus is determined using contact mechanics analysis. Creep and relaxation experiments are performed to characterize the time dependent phenomena of the polymeric surfaces. The surfaces are comprised of epoxy, amine curing agent, and amine coupling agent of systematically varied epoxy-amine equivalence ratios. These ideal interphases model the interphase found in polymer matrix-inorganic reinforcement composites and are used to reveal the relationship between chemistry and nano-mechanical properties. Fourier transform infrared spectroscopy is used to analyze the model interphase chemical composition as a function of amine-epoxy equivalence ratio. The FT-IR analysis and nano-mechanical results are correlated showing how elastic modulus and time dependent properties can be controlled by varying the chemistry and reaction conditions of the system. These data are compared to previously obtained elastic modulus profiles of the interphase in fiber reinforced epoxy matrix composites where the modulus was found to vary by 100% in a ~5 micron region surrounding the reinforcing fibers.

Magnetic Interfaces and Nanostructures
Room 206 - Session MI+NS+NANO 6-ThM

Nanomagnetism

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

8:20am **MI+NS+NANO 6-ThM1 New Directions for Semiconductors***, **D.D. Awschalom**[1],* UC Santa Barbara **INVITED**

PLEASE SEND US AN ABSTRACT. Thank you.

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[1] **Featured Speaker - Science and Technology in the 21st Century**

9:00am **MI+NS+NANO 6-ThM3 Electron Spin Relaxation at Nanometer Length Scales Near a Ferromagnet*, B.C. Stipe*,** *D. Rugar, H.J. Mamin, C.S. Yannoni,* IBM Almaden Research Center*; T.D. Stowe, T.W. Kenny,* Stanford University

Long spin relaxation times will be important to the success of many proposed solid-state quantum computing devices, spintronic devices, and to the detection of single spins by magnetic resonance force microscopy (MRFM). However, spin relaxation may be strongly influenced by thermal magnetic fluctuations in nearby materials such as conductors and ferromagnets. We have employed MRFM with 100 spin sensitivity and 20 nm spatial resolution to study the behavior of E' centers in SiO@sub 2@ near a micron-size ferromagnetic PrFeB particle tip. Magnetic resonance was induced within a 1 nm thick selective slice at 6 GHz and 3 Kelvin in a field gradient of 1 Gauss/nm. For detection, spins were manipulated by adiabatic inversion to produce oscillatory forces on the magnetic particle mounted on a sensitive cantilever. A typical spin ensemble consisted of 2000 spins with a net polarization of 100 µ@sub B@. T@sub 1@ was measured as a function of distance from the tip and was found to systematically decrease from 13 seconds when the spins were far from the tip to about 2 seconds within 500 nm of the tip. We interpret our results in terms of magnetic noise at the spin due to small-angle, thermal magnetic moment fluctuations in the particle. No relaxation effect due to proximity to the sample surface was found for depths greater than 50 nm. This work is supported, in part, by the Office of Naval Research.

9:20am **MI+NS+NANO 6-ThM4 Ferromagnetic Resonance of Monodisperse Co Particles*, M. Farle,*** *U. Wiedwald,* Technische Universitaet Braunschweig, Germany*; M. Hilgendorff, M. Giersig,* Hahn-Meitner-Institut Berlin, Germany

Quasi- twodimensional regular arrays of monodisperse 6 nm diameter Co particles can be produced on Carbon substrates by a monophoretic deposition technique from colloidal suspensions. Transmission electron microscopy reveals hexagonal ordering on micrometer scales for deposition at 0.8 Tesla and a bcc crystalline structure of the particles.@footnote1@ Ferromagnetic resonance (FMR) spectra at 296 K show a weak angular dependence near the paramagnetic resonance field with an easy in-plane magnetization axis . This shows a preferential alignment of the superparamagnetic particles in the film plane. A symmetric lineshape and linewidth dH < 0.1 Tesla is observed which indicates the high monodispersity in magnetic and geometric properties of the individual particles. Characteristic differences of the FMR spectra for different substrates and deposition parameters are observed and will be discussed in terms of simple dipolar coupling models. Supported through EC - grant no. HPRN-CT-1999-00150. @FootnoteText@ @footnote 1@ M. Giersig and M. Hilgendorff, J. Phys. D: Appl. Phys. 32 (1999) L111.

9:40am **MI+NS+NANO 6-ThM5 Magnetic Mirages*, H.C. Manoharan,*** *C.P. Lutz, D.M. Eigler,* IBM Almaden Research Center **INVITED**

While the correlated electron physics underlying the diverse manifestations of magnetism and spin have long been studied via macroscopic behavior, only recently have novel local probes opened the door to a new class of studies on the nanometer length scale. On top of these technological advances, the advent of controlled atomic and molecular manipulation provides a unique opportunity not only to detect spin phenomena at atomic length scales, but to manipulate spins as well. This talk will detail new results that exploit these techniques using low-temperature scanning tunneling microscopy.@footnote 1@ We have directly imaged the electronic perturbation arising from the spin-compensation cloud formed around isolated magnetic moments on a metal surface. Utilizing the detection of this many-body state, known as the Kondo resonance, we demonstrate that the spectroscopic signature of an atom may be sampled and projected to a remote location by means of a surrounding two-dimensional electron gas confined in an engineered nanostructure. The ``quantum mirage'' thus cast by a single magnetic atom can be coherently refocused at a distinct point where it is detected as a phantom atom around which the electronic structure mimics that at the real atom. Once materialized, this phantom can interact with real matter in intriguing ways. We have also been developing a novel communication method based on this effect. @FootnoteText@ @footnote 1@ H. C. Manoharan et al., Nature 403, 512 (2000).

10:20am **MI+NS+NANO 6-ThM7 Correlation of Structural and Magnetic Properties of Ultra-Thin Fe-Films on W(110) by Spin-Polarized STM/STS*, A. Kubetzka,*** *O. Pietzsch, M. Bode, R. Wiesendanger,* University of Hamburg, Germany

To investigate magnetism at the nm-scale and to improve the understanding of its underlying principles, a magnetic imaging technique with ultra-high resolution is of vital importance. Recently, spin-polarized scanning tunneling microscopy/spectroscopy has been developed to a reliable tool to allow such investigations down to the atomic level.@footnote 1,2@ We investigated Fe-films on W(110) at T = 15 K in a coverage range of 1 to 2 ML. In this regime Fe grows as double layer islands interconnected by a closed ML, where the island size can be tuned by the amount of evaporated Fe. By using ferromagnetically coated tips with a magnetization direction along the tip axes, we are sensitive to the out-of-plane component of the sample magnetization. Our measurements reveal that above a critical width of about 2.5 nm along the [1-10] direction, the islands are magnetized perpendicularly to the film plane. Below this width we do not observe a magnetic contrast which we attribute to a reorientation of magnetization to in-plane. Whereas the small perpendicularly magnetized islands are in a single domain state, we observe domain walls above a coverage of 1.5 ML, with wall widths of w = 7±1 nm. @FootnoteText@ @footnote 1@ Pietzsch et al., Phys. Rev. Lett. 84, (2000). @footnote 2@ Heinze et al., Science (accepted).

10:40am **MI+NS+NANO 6-ThM8 Current-driven Magnetization Reversal in Nanopillars*, F.J. Albert,*** Cornell University*; J.A. Katine,* IBM Almaden*; R.A. Buhrman,* Cornell University*; R.H. Koch,* IBM Research Division*; E.B. Myers, D.C. Ralph,* Cornell University

As reported elsewhere, we have successfully fabricated functional F/N/F thin film nanopillar devices with lateral dimensions down to 60 nm, and with one ferromagnetic layer considerably thicker (magnetically harder) than the other. A substantial shape anisotropy has been introduced by patterning a 2 to 1 aspect ratio into these nanopillars. This shape anisotropy is confirmed with the behavior of the measured switching field as a function of angle to the elongated axis. The resistance of these devices shows abrupt, single-domain-like switching when the spin-polarized current flowing through the nanopillar exceeds a critical value and forces the two F layers either into parallel or anti-parallel alignment, depending on the current direction. Here we will report on the results of detailed studies of this spin-transfer switching effect as a function of magnetic field, magnetic orientation and nanopillar composition. Also we will report on the spin-transfer switching dynamics of these devices, measured by probing them with extremely short pulses of current. We are also pursuing the thickness dependence of the switching behavior and will report these results.

11:20am **MI+NS+NANO 6-ThM10 Patterning of Co/Pt Multilayers: Topological vs. Magnetic*, V. Metlushko*,** *G. Crabtree, V. Vlasko-Vlasov, P. Baldo, L. Rehn, M. Kirk,* Argonne National Laboratory*; B. Ilic,* Cornell University*; S. Zhang, S.R.J. Brueck,* University of New Mexico*; B.D. Terris,* IBM Almaden Research Center

Using magnetron sputtering for Pt and e-beam deposition for Co the [Co4/Pt10]n multilayers were prepared on a Si/SiO2 substrate. The patterning of submicron periodic arrays were done in two ways, using traditional interference- or e-beam lithography and lift-off which modulates the material composition of the film, and using 30 keV He ion irradiation through a mask which leaves the chemical composition and topography unchanged but reduces the magnetic anisotropy. The results of systematic characterization of arrays for different doses ranging from 1e15 to 5e16 ions/cm2 with SQUID magnetization to determine the magnetic anisotropy and moment size, with atomic force microscopy (AFM) and magnetic force microscopy (MFM) to determine the topography and the magnetic order in the periodic arrays, and with magneto optical imaging to visualize the moment reversal process during a magnetization cycle will be presented. @FootnoteText@ This work was supported by the U.S. DOE, BES-Materials Sciences, under contract W-31- 109-ENG-38 (V.M., G.C.) and by DARPA (S.Z., S.R.J.B.).

MEMS
Room 309 - Session MM+BI-ThM
Bio-MEMS and Microfluidics

Moderator: P.G. Datskos, Oak Ridge National Laboratory

8:20am **MM+BI-ThM1 Microfabrication Technologies for Biomedical Applications***, **M. Ferrari,*** The Ohio State University **INVITED**
PLEASE SEND US AN ABSTRACT. Thank you.

9:00am **MM+BI-ThM3 Suppression of Blood Serum Adhesion on Quartz Inner Wall of Microcapillary Coated by Bio-compatible MPC Polymer***, H. Ogawa, A. Oki, **Y. Takamura**, S. Adachi,* The University of Tokyo, Japan*; T. Ichiki,* Toyo University, Japan*; K. Ishihara, Y. Horiike,* The University of Tokyo, Japan

We are developing the healthcare device which enables us to detect various health markers from trace amount of the blood. To suppress adhesion of proteins in a blood injected into a quartz made microcapillary, the 2-methacryloyloxyethylphosphorylcholine (MPC) polymer which is now utilized to artificial blood tube, contact lens, in-vivo sensors, etc. has been coated on the inner wall, thus leading to bio-compatibility of the quartz surface. A microcapillary with a 30 x 30 µm cross-section and 10 mm in length was fabricated in a 2cm x 2cm quartz chip by dry-etching and subsequent press-bonding of a cover quartz plate in 1% HF solution. A pH=7.4 phosphate buffered solution (PBS) was filled in the capillary and the serum was injected from one end by electroosmosis pumping. The concentrations of proteins, which were monitored by 220nm UV absorption at the point of 4mm apart from the injection, rose up rapidly when the serum arrived at this point and then were kept at a constant value in the 3 wt% MPC coated capillary, while those in uncoated capillary were decreased gradually by adhesion of proteins on the inner wall after showed maximum. To investigate the interaction of proteins with the MPC polymer coated surface, FTIR-ATR spectra for MPC coated and uncoated wall surfaces exposed by a blood serum were measured. The adsorption peaks by NH@sub x@ and C=O of proteins in the uncoated surface increased with exposure time, while the proteins did not absorb on the coated surface. These results clearly demonstrate the excellent bio-compatiblity of the MPC polymer for a blood handling capillary chip.

9:20am **MM+BI-ThM4 Biologically-Compatible Polymeric MEMS Devices Fabricated using Holographic Two-Photon Induced Photopolymerization***, **L.L. Brott**,* Technical Management Concepts, Inc.*; S.M. Kirkpatrick,* Science Applications International Corporation*; M.O. Stone,* Wright-Patterson Air Force Base

Research in the bio-MEMS field has been driven by the desire to reduce the time, complexity and equipment needed to carry out clinical diagnostic procedures. Current bio-MEMS strategies rely extensively upon externally added reagents and conventional photolithography in the fabrication of these systems. In an effort to simplify these devices even further, research has begun incorporating the reagents, i.e. enzymes, directly into the walls of the microfluidic channels. Consequently, a new polymeric material based on poly(ethylene glycol) which maintains the biological activity of the reagents and is not sensitive to aqueous environments, yet whose monomeric form accepts aqueous solutions, was developed. The microfluidic channels were patterned by photocuring the monomer using a two-photon initiated photopolymerization process at 800 nm. A rose bengal/triethanol amine initiator system was used. By using a laser as the light source, holograms were patterned onto the device resulting in well defined and complex patterns.

9:40am **MM+BI-ThM5 Patch Clamping with Microfabricated Planar Electrodes***, **K.G. Klemic**, J.F. Klemic, M.A. Reed, F.J. Sigworth,* Yale University

The patch clamp technique is the most sensitive way to record the small ionic currents carried by ion channels and transporters in cell membranes. To make a typical recording, the ~1 micron tip of a glass or fused-quartz micropipette, filled with saline solution, is sealed over a patch of cell membrane, electrically isolating it with a very large electrical "seal resistance" of 10-100 G@ohm@. Here we describe the first use of new materials and a new configuration for patch-clamp electrodes. We have microfabricated planar electrodes that mimic the shape of the tip of the micropipette by aniostropic etching of single crystal quartz or by micromolding the silicone elastomer, poly(dimethylsiloxane) (PDMS). The planar geometry has several advantages over the standard glass micropipette currently used for patch clamp recording. First, it permits direct integration of the first stage of amplification electronics into the electrode. Second one electrode can be easily scaled to an array of electrodes for simultaneous patch-clamp recordings from many cells, greatly expanding the discovery of new ion channel genes and new pharmacological agents directed to ion channel targets. Third, microfluidic channels can be integrated to permit fast solution exchange on both sides of the membrane, something that is not presently possible. Lastly, the electrode is designed to have a small solution volume that reduces the capacitance and thereby reduces by an order of magnitude the contribution of the electrode to the background noise. The design and fabrication of these novel patch electrodes as well as membrane current recordings using these devices will be presented.

10:00am **MM+BI-ThM6 High Sensitivity Resonant Biosensor***, **B. Ilic**, D. Czaplewski, H.G. Craighead,* Cornell University*; P. Neuzil,* Institute of Microelectronics, Singapore*; C. Campagnolo, C. Batt,* Cornell University

There is a growing demand to produce highly selective biological sensors for the detection of small quantities of biological microorganisms using micromachining. In this work, the detection of bacteria using a resonant frequency based mass detection biological sensor has been accomplished. The biological sensor under development consists of an array of resonating cantilever beams fabricated, using bulk silicon micromachining techniques, from both low pressure chemical deposition (LPCVD) and plasma enhanced chemical vapor deposition (PECVD) low stress silicon nitride. For this experiment an array of cantilevers with dimensions of varying length from 15µm to 500µm, varying width of 2µm to 20µm, thickness of 320nm for the LPCVD, and t=600nm for the PECVD nitride, were used. Escherichia coli O157:H7 antibodies were immobilized on the surface of the resonators. Devices were subsequently exposed to varying concentrations of E. Coli cells in solution and any loosely bound cells were removed. In order to determine the mass bound to the cantilever, a frequency spectra was taken before and after the binding of the cells to the cantilever. Signal transduction of the micromechanical oscillators has been accomplished by measuring the out of plane vibrational resonant mode with an optical deflection system. The measured vibrational mode was entirely due to thermal noise and ambient vibrations in air. The measured resonant frequency shift as a function of the binding of additional cells was observed and correlated to the mass of the specifically bound E. Coli O157:H7 cells. Our results indicate good agreement with the predicted theory of linear elasticity. Under ambient conditions where considerable damping occurs, we were able to detect single E. Coli cells. Methods, utilizing vacuum encapsulation and tailoring of the cantilever dimensions, for single molecule detection will be discussed.

10:20am **MM+BI-ThM7 Nanofluidic Entropic Trap Array device for DNA Separation***, **J Han**, H.G. Craighead,* Cornell University

A nanofluidic entropic trap array device@footnote 1@ for separation and analysis of long DNA molecules was constructed and tested. The device contains many constrictions (entropic traps) with dimensions smaller than the radius of gyration for the DNA molecules. The length dependent trapping of DNA and resulting electrophoretic mobility difference enables efficient separation of DNA in the range of 5kb ~ 200kb, typically within 30 minutes, in a channel as short as 15 mm without using a gel.@footnote 2@ We fabricated devices with multiple channels with the same structural parameters, for a parallel analysis of samples. Multiple DNA samples were separately introduced into the device and collected into narrow bands for launching. The amount of DNA in the launching band could be electrically controlled. Simultaneous separation of multiple samples enables one to compare electrophoregrams for calibration or direct comparison for applications such as DNA fingerprinting. A range of device parameters were tried, and the optimization of the device will be discussed. @FootnoteText@ @footnote 1@ J. Han and H. G. Craighead, J. Vac. Sci. Tech. A, 17, 2142 (1999) @footnote 2@ J. Han and H. G. Craighead, Science, in publication (2000)

10:40am **MM+BI-ThM8 Integration of Microcapillary Electroporesis and Inductively Coupled Plasma Spectrometry for Rapid Biological/Chemical Analysis***, **T. Ichiki**, T. Koidezawa, R. Taura, T. Ujiie,* Toyo University, Japan*; Y. Horiike,* The University of Tokyo, Japan

Rapid and sensitive elemental specification of trace amounts of samples are important for chemical, biological, environmental and clinical applications. For the goal of integration of microcapillary electrophoresis (µCE) and inductively coupled plasma (ICP) optical emission spectrometry (OES) on a chip, we have fabricated µmCE chips with a nebulizer, and have investigated conditions for generating microscale ICPs. Microcapillary and nebulizer patterns were etched onto the quartz plate in C@sub 4@F@sub 8@/SF@sub 6@ plasmas using Cr masks. The etched quartz plate was dipped in 1% diluted HF solution and then bonded together with the other quartz plate with drilled holes. These two plates were press-bonded under the load of 1.3 MPa at room temperature for 24 hours. Samples separated via electroosmotic and electrophoresis phenomena were nebulized by controlling the carrier gas flow around the nozzle located at the capillary end to achieve the injection of pico-liter droplets in the gas. Subsequently, generation of microscale VHF-ICPs was investigated. Discharge chambers of 500µm-5 mm depth and/or width were fabricated on 20 mm@super 2@ quartz plates, which was attached under the 70-mm-@phi@ circular quartz plate set on a small vacuum chamber. A 5-mm-@phi@ antenna was set on the circular quartz plate so as to locate just above the discharge chamber. The power for Ar plasma ignition and mode jump from E- to H-discharge was examined by means of spectroscopy. In the case of discharge chamber dimension of 5 mm width and more than 2 mm depth, the power for ignition was only 5 W at pressures of 0.01-1 Torr, while no mode changes were observed even at 100 W. When reducing the discharge chamber depth to 1-1.5 mm, mode change occurred around 10 W and emission intensity drastically increased by 100 times. Thus high density VHF-ICP was found to be easily attained when the characteristic length of the discharge space is around 1 mm and the pressure is 1-10 Torr.

11:00am **MM+BI-ThM9 Silicone Elastomer Microwell Arrays for High Throughput Protein Biochemical Assays*, J.F. Klemic*,** *H. Zhu, M.A. Reed, M. Snyder,* Yale University

The identification of the function of large numbers of gene products is an important challenge in post-genomic research. Inexpensive, disposable microwell arrays have been developed for high throughput screening of protein biochemical activity. The microwell arrays are cast in silicone elastomer sheets and placed on top of microscope slides for compatibility with commonly available sample handling and recording equipment. Arrays consist of high density (hundreds per slide), small volume (~300nl) wells which permit high throughput batch processing and simultaneous analysis of many individual samples using only small amounts of protein. Device utility has been demonstrated through the simultaneous analysis of 120 protein kinases from Saccharomyces cerevisiae assayed for phosphorylation of 17 different protein substrates. These microwell arrays, as tested, permit the simultaneous measurement of hundreds of protein samples, however, the use of micromolded silicone elastomer allows array densities to be readily increased by several orders of magnitude. With the further development of appropriate sample handling and measurement techniques, these arrays may be adapted for the simultaneous assay of several thousand to millions of samples.

11:20am **MM+BI-ThM10 Development of a Micro Capillary Pumped Loop System for Microelectronic Device Cooling*, H. Yun*,** *H. Lee, K. Cho, I. Song,* Samsung Advanced Institute of Technology, South Korea

Increasing demand for processing data leads to faster clock speeds and large integration. As a result, the heat generation of microelectronic devices is increasing at rapid rate. Current PCs generate 20~30 Watts/cm@super 2@ of heat. If this trend continues, 100 Watts/cm@super 2@ of heat generation are expected within few years. Since conventional phonon diffusion based metal heat sinks can handle only up to 10 Watts/cm@super 2@, an alternative cooling technology is desired. In this paper, a micro capillary pumped loop (CPL), which is a microfabricated, capillary pressure driven fluid cycle is proposed as an alternative means of cooling microelectronic devices with large heat generation. The heat is absorbed at the evaporator by vaporizing the circulating fluid, and released out of the system at the condenser. The capillary forces of the microfabricated wick structure at the evaporator drives the fluid. Since the fluid particle directly carries the heat out of the system, the micro CPL is expected to be more effective than the conventional diffusion-based heat sinks. A prototype of 30 Watts/cm@super 2@ cooling capacity has been built and tested. Microchannels have been etched on a silicon wafer to form the evaporator and the condenser. The prototype operated successfully under 30 Watts/cm@super 2@ heat flux while keeping the junction temperature below 400K. The maximum heat flux was 50 Watts/cm@super 2@ before the dryout at the evaporator occurred. A nonlinear dynamic model has been developed to simulate the interaction between various components of the micro CPL. The simulation model successfully captured the overall trends of the experimental data. Further research on the underlying physics are desired for better understanding of this device.

11:40am **MM+BI-ThM11 Design, Fabrication, and Testing of Cross Flow Micro Heat Exchanger*, C.R. Harris*,** *M. Despa, K.W. Kelly,* Louisiana State University

A cross flow micro heat exchanger was designed and fabricated to maximize heat transfer from a liquid to a gas (air) for a given frontal area and pressure drop of each fluid. To accomplish the goal of high heat transfer, micro channels with scales ranging from 200 µm to 500 µm were utilized. By constraining the flow to narrow channels, heat transfer is enhanced since the convective resistance at the solid/fluid interfaces is reduced. To minimize the pressure drop associated with micro channels, air passes through the plane of the heat exchanger via thousands of parallel short channels. Heat is transferred to the air from liquid that passes in cross flow through tens of parallel channels. Predicted design performance for plastic, ceramic, and aluminum micro heat exchangers are compared to one another and to current innovative car radiators. The micro heat exchangers can transfer greater heat per mass or volume than existing heat exchangers within the context of the design constraints specified. Important applications of this technology include automotive, home heating, and aerospace fields. The heat exchanger designed for plastic was fabricated by aligning and bonding two identical polymer (PMMA) parts that had been embossed using the LIGA process. After heat exchanger assembly, liquid was pumped through the heat exchanger with no leaks. Heat transfer and pressure drop tests were performed on the fabricated polymer heat exchanger. The experimental data is compared to the design calculations and to other heat exchangers.

Manufacturing Science and Technology
Room 304 - Session MS-ThM

Advanced Modeling and Control for IC Manufacturing

Moderator: S.S. Shankar, Intel Corporation

8:20am **MS-ThM1 Simulation of Transient Enhanced Diffusion of B in Si*, G.S. Hwang*,** *W.A. Goddard III,* California Institute of Technology

Ever shrinking device dimensions requires the formation of ultrashallow junctions with high concentrations of electrically active dopants and box-like profiles in order to maximize drive currents while minimizing short channel effects. To control such junction properties it is necessary to understand quantitatively (i) the underlying mechanisms of transient enhanced diffusion (TED) of dopants and (ii) the dynamics of defect/dopant clustering during implantation and postimplantation annealing. We present a systematic approach to address such issues in which we combine (i) kinetic Monte Carlo (kMC) mesoscale simulations capable of describing the length and time scales of TED with (ii) quantum mechanics [density functional theory (DFT)] calculations of the fundamental atomic level processes and (iii) experimental validation. In recent years much effort has been devoted to understanding the TED of B in Si; however, most studies have been performed using moderate energy (~40 keV) Si@super +@ implants into MBE-grown B-doped layers. The dominant mechanisms of the B TED based on this previous work may not be dominant for the low energy (10@super 20@ cm@super -3@) inherent to ultrashallow junction fabrication. In this talk, we will present (i) new mechanisms of B clustering and (ii) strain-induced defect-defect and defect-dopant interactions, and discuss how crucial it is to have such detailed information for accurately predicting the doping profiles in ultrashallow junction processing. We will also address several unresolved issues in the low-energy and high-concentration regime: (i) the validity of '+1' model, (ii) the surface proximity effect, and (iii) the role of defect/dopant clustering in determining junction profiles.

8:40am **MS-ThM2 New Physics for Models of Transient Enhanced Diffusion***, M.Y.L. Jung,* ***E.G. Seebauer,*** University of Illinois, Urbana-Champaign

As device dimensions continue to shrink, the constraints on processing imposed by Mother Nature become ever more stringent. The optimization of chemical kinetics and mass transport is therefore playing an increasingly important role in defining and widening process windows. Here we discuss TCAD modeling of transient-enhanced diffusion (TED) after ion implantation during ultrashallow junction formation by rapid thermal annealing. TED has long been modeled using a large set of reaction-diffusion equations for the dopant, point defects, and extended defects. However, current commercial and public-domain SUPREM-based software mishandles several important aspects of the reaction-diffusion network. For example, many of the diffusivities are inappropriately parameterized. Also, the software lacks a self-consistent, time-dependent treatment of

Poisson's equation and therefore miscalculates the electric-field-driven drift of charged defects. There are further problems: even the best TED models neglect important effects of the nearby free surface and of intense illumination. For example, there is no incorporation of near-surface band bending, of changes in charged defect concentration during illumination, or of enhancement of point defect motion though local energy dumping by e-h recombination. This talk outlines how such effects can be incorporated and discusses conditions under which they are likely to be important.

9:00am **MS-ThM3 Fast-Ramp Annealing for Reducing Implant-Induced Transient Enhanced Diffusion***, **M.Y.L. Jung**, R. Gunawan, R.D. Braatz, E.G. Seebauer,* University of Illinois, Urbana-Champaign

Some experimental evidence has accumulated in recent years to support the use of "spike anneal" temperature trajectories with very fast heating and cooling rates for making ultrashallow junctions by ion implantation. Improved device properties have been claimed using heating rates of 400 C/s or more. This procedure supposedly optimizes junction depth and sheet resistance by reducing transient-enhanced diffusion (TED) of the dopant. However, the theoretical justification for using such fast ramps has been weak. Since the design and use of fast-ramp annealing tools will require substantial investments by equipment manufacturers and IC manufacturers alike, it is important to confirm by TCAD modeling the existence and potential magnitude of such effects. TED has long been modeled using a large set of reaction-diffusion equations for the dopant, point defects, and extended defects. However, current commercial and public-domain SUPREM-based software mishandles or ignores several important aspects of the reaction-diffusion network. We briefly discuss how we have fixed these problems, focusing in particular how proper incorporation of surface oxidation or nitridation kinetics closely couples the gas ambient in the annealer to dopant motion down near the junction within the Si bulk. We then show how variations in heating and cooling rates can be used to favor or disfavor important reaction-diffusion pathways within the overall system of effects that governs TED. In particular, we point out how the widely-used contant-temperature annealing step near 500 C for pyrometer calibration actually influences subsequent profile evolution in a profound way.

9:20am **MS-ThM4 Dynamic Simulation: Guiding Manufacturing from Process Mechanisms to Factory Operations***, **G.W. Rubloff**,* University of Maryland **INVITED**

Dynamics plays a critical role in the behavior and performance of semiconductor manufacturing from the unit process level to full factory operations, yet major gaps exist in our ability to simulate the consequences of this dynamics. At the process level, process models can provide a reasonable description of steady-state process behavior, but the realities of semiconductor equipment dictate that both total process times and thermal histories depend on the dynamics of the equipment and control systems, as well as on the raw process itself. We have developed physically-based dynamic simulation strategies which accurately reflect time-dependent behavior of equipment, process, sensor, and control systems, and we have used them to understand and optimize equipment systems and process recipes. Another dimension of dynamics appears in the behavior of cluster tools, where the tool architecture, process module populations, and scheduling algorithms add further dynamics to tool behavior. We have integrated reduced-order process models, reflecting dynamic unit process simulations, with discrete event simulations of cluster tool performance to enable co-optimization of process recipes, cluster tool configurations, and their scheduling algorithms. Finally, we have incorporated these integrated models into factory-level operational models to facilitate the evaluation of factory-level performance as a function of process, equipment, and logistics choices. These simulation strategies seem attractive in terms of their ability to represent dynamics, from continuous parameter dynamic recipes at the unit process level, to discrete-event dynamics associated with scheduling and throughput at the factory level.

10:00am **MS-ThM6 Integrated Metrology with Run to Run Control***, **P.R. Solomon**, P.A. Rosenthal, S. Bosch-Charpenay, J. Xu, W. Zhang,* On-Line Technologies, Inc. **INVITED**

The semiconductor industry is moving to adopt copper/low-k interconnect technology, smaller critical dimensions and 300 mm wafers. Many of these changes require tightening of the process specifications. Introducing these changes while maintaining product quality and reducing costs is a formidable challenge. Especially important are low-k dielectrics, chemically amplified resist, FSG and BPSG films that require control of their chemical composition as well as thickness. Integrated metrology with run-to-run control can facilitate the introduction of these new technologies because of its ability to improve process control while at the same time reducing manufacturing costs. Such benefits can be achieved for most current process steps as well. This paper will review some early success stories for Epi silicon and CMP processes. The integrated metrology for Epi employs an FTIR based film thickness monitor with model based analysis, integrated onto the cooldown chamber of the cluster tool for 100 % multi-point measurement and control. The FTIR is also applicable to the monitoring of thin film chemical composition. While FTIR has been widely used in R&D environments, its application to mainstream production metrology and process monitoring on product wafers has historically been limited by: 1) the optical complexity of film stacks used in production, 2) sample-dependent backside reflection artifacts caused by substrates which are transparent in the infrared, and 3) the lack of robust models of the chemically variable optical constants of modern IC materials. These limitations have been eliminated in a series of recent FTIR technology advances. The paper considers these recent advances, how the technology is integrated with the processing tools, the operation of the system, the improvement in the product and the cost of ownership. The paper will also examine the metrology available for integration and the future course for making such technology widely available, including standards for integration and methods for delivering the technology.

10:40am **MS-ThM8 W CVD Thickness Metrology and Run-to-Run Control using Mass Spectrometry***, **Y. Xu**, T. Gougousi, R. Sreenivasan, G.W. Rubloff, J.N. Kidder, E. Zafiriou,* University of Maryland

For a H2/WF6 CVD process for selective W deposition in an Ulvac cluster tool, mass spectrometry has been used to observe HF product generation and H2 depletion. HF signal was proportional to the deposited W thickness to about 7%, providing an in-situ thickness metrology as a candidate to drive run-to-run thickness control. To assess this possibility, a systematic temperature drift of -50C per wafer was introduced, which in the absence of control would cause the film thickness to decrease by 40-50% over a ten wafer lot. Using a robust control algorithm to maintain a constant integrated HF mass spec signal by adjusting the nominal deposition time, the effect of the temperature drift on deposited film thickness was largely compensated, and the W film thickness was maintained within 10% of the target value. The metrology accuracy was limited by the low (about 3%) reactant conversion rate of the process, coupled with significant background signals. Since blanket W CVD processes as employed in manufacturing achieve much higher conversion efficiencies (40-50%), we anticipate considerable improvement in the efficacy of metrology and control in these situations. Our results, and their projection to realistic manufacturing scenarios, present an encouraging opportunity to use in-situ chemical sensing for process metrology and control.

11:00am **MS-ThM9 Feedback Control of Morphology During III-V Semiconductor Growth by Molecular Beam Epitaxy@footnote 1@***, **R.L. Kosut**, J.L. Ebert, S. Ghosal,* SC Solutions*; R. Caflisch,* University of California, Los Angeles*; M. Gyure, J.J. Zinck,* HRL Laboratories

This paper addresses the modeling and control of epitaxial growth of III-V semiconductor material by Molecular Beam Epitaxy. In layer-by-layer growth mode, oscillations and envelope decay in the specular intensity of the reflection high energy electron diffraction (RHEED) pattern have been correlated to the instantaneous density of steps on the surface. This allows for the possibility of in situ monitoring and control of surface morphology during growth. A control algorithm and strategy was first developed using a KMC simulation model of III-V growth together with dynamic thermal models of the effusion cells and cracker valves. The strategy discovered from the simulations was to control growth layer-to-layer which turns out to have two important features: (1) it is very robust to chamber variations and uncertainties, and (2) the resulting form of the system is well modeled as a discrete-time system where sample times are replaced by layer number. There is a vast body of control theory which can be applied to such systems. The control was implemented on the MBE system to control RHEED oscillations and decay rates in real-time during III-V growth in HRL Laboratories MBE chamber. The RHEED signals were used to estimate oscillation period which was compared to a reference and the error was used in a control algorithm to adjust, in real-time, the set-point temperature of the III material effusion cell. The RHEED signals were also used to estimate oscillation decay and then used to adjust the V material cracker valve opening. Simulations compared well with experimental data in both open and closed loop. Investigations are currently under way to use a photoemission (PE) sensor in place of the RHEED sensor. Hopefully results will be available at the time of the AVS conference. @FootnoteText@ @footnote 1@ Research supported by DARPA, Applied Computation & Mathematics Program.

11:20am **MS-ThM10 Data Requirements and Communication Issues for Advanced Process Control***, **R.J.M. Markle,** E.C.J. Coss, Jr,* AMD **INVITED**

Data streams and communication issues are the most critical areas for successful Advanced Process Control (APC) programs. These areas are vital for both APC run-to-run controllers and Fault Detection and Classification (FDC) systems used for high volume manufacturing applications in the semiconductor industry. All APC systems rely on data streams to make their process changes, to keep the process on target and in control, and to otherwise signal a need for engineering involvement to make similar corrective actions. The access to, communication of, and reliability and integrity of these data streams are essential to all APC programs. APC run-to-run controllers use the data to make changes in the process. FDC systems focus on predicting pending equipment- or process- related problems or detecting them quickly when they occur. The inability to access the needed data stream can prohibit the use of APC run-to-run controllers or FDC systems on critical process operations. Worse yet, the use of unreliable or corrupted data can cause undesirable consequences. In order to better capitalize on the improvements demonstrated with APC run-to-run controllers and FDC systems, end users have often had to create their own communication and data processing methods. The first decade of the 21st century will place increased demands on process and metrology equipment manufacturers, APC software and hardware suppliers, and APC programmers. Improvements in these areas through the use of industry standards and best known methods could greatly accelerate the APC field. Wafer-to-wafer and within wafer process control could be essential for 300 millimeter wafer and large flat panel processing will need these improvements. We will discuss examples that Advanced Micro Devices (AMD) experienced in Fab25 within the past year. The case studies relate to complex but necessary methods to get the data we need for a FDC system and the role of metrology data on APC run-to-run controllers. Data and communication requirements for the next three to five years will also be discussed. The increased demands on current process and metrology systems will increase as we begin to use new and alternative technologies to support more advanced APC strategies.

Processing at the Nanoscale/NANO 6
Room 302 - Session NS+NANO6-ThM

Nanostructured Materials

Moderator: T. Michalske, Sandia National Laboratories

8:20am **NS+NANO6-ThM1 Implantation and Pinning of Size-selected Ag Nanoclusters at the Graphite Surface***, S. Pratontep, S.J. Carroll, M. Streun, P.D. Nellist,* ***R.E. Palmer,*** The University of Birmingham, UK*; S. Hobday, R. Smith,* Loughborough University, UK

Size-selected nanoclusters provide building blocks for creating nanoscale structures. However, the deposition of such clusters on surfaces is often susceptible to surface diffusion and thus aggregation of clusters. We have investigated the deposition of size-selected Ag@sub N@@super +@ clusters (N=20-200) on graphite at elevated impact energies (E=0.25-6 keV). Molecular dynamics simulations establish two energy regimes in which lateral diffusion of the deposited clusters is inhibited.@footnote 1@ At high impact energies (> 20 eV/atom) the clusters are found to penetrate into the surface and come to rest at the bottom of an open tunnel so created. The implantation depth is found to vary linearly as E/N@super 2/3@. This implies a constant decelerating force which is proportional to the cross-sectional area, rather than the volume, of the cluster. At lower impact energies (~10 eV/atom) we have found a size-dependent threshold energy above which the cluster is pinned on the surface at the impact site via the creation of a point defect. This threshold exhibits a linear dependence with the cluster size, N. This prediction is confirmed by scanning tunnelling microscopy (STM) investigations of cluster pinning as a function of cluster size and impact energy. Both the implantation and the pinning behaviour suggest viable methods for the fabrication of well-defined nanostructured surfaces. @FootnoteText@ @footnote 1@ S.J. Carroll, P.D. Nellist, R.E. Palmer, S. Hobday and R. Smith, Phys. Rev. Lett. 84, 2654 (2000).

8:40am **NS+NANO6-ThM2 Self-organization of Pt Nanoparticles on Surfaces in Catalytic Reaction***, **Q.-H. Hu,** B. Kasemo,* Chalmers University of Technology, Sweden

Small metal particles have long been used as catalysts in heterogeneous catalytic reactions. The carrier may act both as a physical support and promoter for the catalytic reactions. Recently it is realized in the Monte Carlo simulation that supported cat alyst particles may self-organize through a rather complex interaction with the supported surface and gaseous species in the reaction environment. As consequence, individual particles may attain different shape(adsorbate-induced reshaping or facetting) an d combination of facets that strongly influence the reaction kinetics. In addition, particles as a whole may adopt different spatial arrangement, which affects mass-transport in the reaction. We report a technique for preparing SiN-membrane and TEM observ ations of self-organization of Pt nanoparticles on the membrane in the catalytic reaction. The TEM of as-prepared samples 'Pt deposited on the membranes' showed three types of morphology, continuous granular film at the nominal thickness of above 20 nm, irr egular-shaped drops of varied sizes and coverage below 5 nm, and semi-continuous films with varied density of cracks at the thickness in between. The TEM of the samples heat-treated in the ambience of H2 and O2 at atmospheric pressure showed significant c hange in morphology. Thin Pt samples treated at 300 °C and H2/O2=0.4 self-organized into short-range ordered nanoparticles of less than 5 nm in size with a comparable interparticle spacing. The particle size is proportional to the initial thickness. On the medium thickness samples, multi-connected irregular-shaped islands resulted. The width of the interconnection is about 10 nm and almost equal to the spacing between the islands. Recrystalization of Pt was also observed. A systematic variation of treatment conditions on samples of different thickness, together with the evaluation of the catalytic activity is currently undertaken to realize a controlled shape of the self-organized particles.

9:00am **NS+NANO6-ThM3 Quantum-Coherence and Self-Assembly of Metallic Nanostructures***, **H. Brune,*** Ecole Polytechnique Federale de Lausanne, Switzerland **INVITED**

We will discuss several means for the self-assembly of metallic islands of well defined size and mutual distance. The surface states of the (111)-oriented transition metal surfaces have extremely small Fermi vectors leading to long wavelength quantum-interference patterns. For Cu/Cu(111) these Friedel oscillations give rise to long range oscillatory adsorbate-adsorbate interactions which can be used to arrange adatoms or islands in hexagonal patterns. The period of these superlattices is @lambda@@sub F@/2 and thus coherently reflects the surface electronic properties. We then present the growth of nanostructure arrays using kinetically controlled growth on dislocation networks serving as templates. The mean size of the Ag, Fe, and Co dots is adjusted by the coverage. Their size distribution is given by the statistics of deposition. It has a half width at half maximum of 12% at 0.10ML, which is competitive with state-of-the-art semiconductor quantum dots, and goes down to 4% at 0.5ML. Small Co islands with well defined sizes can be created through coarsening by cluster diffusion on Pt(111). Since each cluster size has its own onset temperature for diffusion one can deliberately adjust the mean island size by the annealing temperature giving rise to high densities of very small islands ideally suited to investigate size-effects on reactivity and magnetic moment per atom.

9:40am **NS+NANO6-ThM5 Immobilization and Isolation of Molecule Corral Nanostructures Produced on Highly Oriented Pyrolytic Graphite***, **J.D. McBride,** Y.J. Zhu, B. Van Tassel, R.C. Jachmann, T.P. Beebe, Jr.,* University of Utah

Gold and silver nanostructures have been produced by condensing evaporated gold onto nanometer-sized etch pit templates (molecule corrals) on the surface of highly oriented pyrolytic graphite (HOPG). By varying the ratio of the thickness of gold deposited to the diameter of the etch pit templates, three distinct types of gold nanostructures can be produced: rings, disks, and mesas. These nanostructures have been formed with their outer diameters ranging from 20 to 150 nm. In order to use these nanostructures in the microelectronics industry, or for potential use as sensor arrays, they must be isolated both from one another as well as from the conductive graphite surface on which they are produced. Two different methods for isolating these nanostructures have been investigated. First, the use of (3-mercaptopropyl)trimethoxysilane (MPS) as a molecular adhesive@footnote 1@ to anchor the gold nanostructures to glass and silicon substrates was evaluated. The degree of gold transfer to the glass and silicon surfaces was examined using x-ray photoelectron spectroscopy (XPS), time-of-flight secondary ion mass spectrometry (ToF-SIMS), scanning tunneling microscopy, and atomic force microscopy. The second technique used for isolating gold nanostructures was the immobilization and encapsulation of the nanostructures within a spin-coated fluoropolymer film. These polymer films were examined using both the spectral and imaging modes of XPS and ToF-SIMS. @FootnoteText@ @footnote 1@ Goss, C. A.; Charych, D. H.; Majda, M. Anal. Chem. 1991, 63, 85-88.

10:00am **NS+NANO6-ThM6 Ultraflat Nanosphere Lithography*, W. Frey*,** *A. Chilkoti,* Duke University

Easy fabrication of periodic features on the submicron scale is needed for many applications ranging from surface-enhanced spectroscopy to quantum structures and nanostructured biofunctional surfaces. For example, biosensors require nanopatterns to be stably bonded to the substrate in solvents, as well as capable of subsequent functionalization by self-assembly chemistry. Additionally, for the study of cell surface-interactions, the nanopatterned surface should have minimal height variation in order to decouple physico-chemical and topographical effects on cell behavior. We have therefore designed a new method, ultraflat nanosphere lithography (UNSL), to create periodic nanopatterned surfaces of well-defined size and minimal topography for different materials that are also stably bonded and are capable of self-assembly chemistry. UNSL is based on nanosphere lithography@footnote 1@ and ultraflat template stripping.@footnote 2@ Nanospheres are self-assembled into close packed hexagonal arrays on mica. Material M1 is evaporated through the mask formed by the self-assembled spheres. After the spheres have been lifted off the substrate, evaporation of material M2 embeds the nanopattern in a much thicker matrix. A silicon or glass substrate is glued to the surface for mechanical support. Finally, the mica is stripped off, revealing an ultraflat pattern of nanotriangles of M1 embedded in M2. In order to demonstrate the feasibility of UNSL, we have chosen pairs of materials M1 (Au, Ag) and M2 (Al, SiO) so that each can be independently functionalized by orthogonal self-assembly, and transparent samples as well as insulator-conductor pairs can be created. We have visualized the nanopatterns fabricated by UNSL using AFM, SEM and Auger electron imaging, and demonstrate that the surface roughness is below 1 nm (rms) over areas of several hundred µm@super 2@. @FootnoteText@ @footnote 1@Deckman, et.al.: Appl. Phys. Lett. 41, 377 (1982)@footnote 2@Hegner, et.al.: Surf. Sci. 291, 39 (1993)

10:20am **NS+NANO6-ThM7 Controlled Growth of Metal Nanoclusters on Polymers*, V. Zaporojtchenko*,** *K. Behnke, A. Thran, T. Strunskus, F. Faupel,* University of Kiel, Germany

Metal nanoparticles dispersed on a polymer surface as well within a polymeric matrix offer interesting electronic, optical and catalytic properties due to their small dimensions.@footnote 1@ For metals with moderate reactivity the high cohesive energy of the metal in combination with the weak metal-polymer interaction leads to metal aggregation on the surface. The nucleation and growth of noble metals (Cu, Ag, Au) as well as more reactive metals (Ni, Cr) onto fully cured polymer films with different composition are considered. The metal deposits which were prepared in situ by physical vapor deposition were characterized by combination of transmission electron microscopy (TEM), atom force microscopy (AFM), x-ray photoelectron spectroscopy (XPS) and a novel very sensitive radiotracer technique.@footnote 2@ An extreme variation in metal condensation behavior was observed on the different polymers. It appears to be related to the polymer surface energy and suggests a connection between macroscopic wetting and atomic condensation. The effect of metal-polymer interaction as well as the deposition parameters and surface pretreatment on the nucleation process has been investigated in order to understand how the morphology of the metal deposit can be affected. Influencing the basic processes@footnote 3@ occuring in the initial stages of metal-polymer interface formation it is possible to form 2-d metal nanoparticle-polymer composits with a large variation of the metal cluster size and metal cluster density on the polymer surface. @FootnoteText@ @footnote 1@ Metal Clusters, ed. by W. Ekardt, John Wiley & Sons, Chichester, England 1999. @footnote 2@ A. Thran, M. Kiene, V. Zaporojtchenko and F. Faupel, Phys. Rev. Lett. 82, 1903 (1999). @footnote 3@ V. Zaporojtchenko, T. Strunskus, K. Behnke, M. Kiene, and F. Faupel, J. Adesion Sci. Technol., 14(3), 467 (2000).

10:40am **NS+NANO6-ThM8 Noble Metal Nanoparticles in Polymeric Thin Films**, *M.K. Chilton,* ***P.G. Van Patten,*** Ohio University

Recent results obtained in our laboratory and elsewhere have demonstrated the possibility of using noble metal nanoparticles to enhance the emissive response from phosphor materials by more than an order of magnitude. We have employed electrostatically-grown polymer-based thin films as model systems for a series of experiments on these light-emitting nanocomposites. The fabrication and characterization of these model thin films will be described in detail along with spectroscopic results from the phosphor films. The enhancement effect has thus far only been observed in trivalent lanthanide ions. Experimental results suggest that the enhancement mechanism is related to the field focussing properties of the nanoparticles. Localized field enhancement apparently leads to the introduction of odd parity terms into the transition matrix element for photoabsorption. Interestingly, the rate of spontaneous emission from the ions are not observed to change as a result of the nanoparticles' presence. A detailed hypothesis for the mechanism will be presented consistent with existing photophysical evidence. The implications of the enhancement phenomenon for device development will also be discussed.

11:00am **NS+NANO6-ThM9 Biomimetic Self-Assembly*, G. Stucky*,** University of California, Santa Barbara **INVITED**

PLEASE SEND US AN ABSTRACT. Thank you.

11:40am **NS+NANO6-ThM11 Cluster Size Effect Observed for Gold and Silver Sulfide Nanoparticles Synthesized by Sol-Gel Technique as Studied by X-ray Photoelectron Spectroscopy*, S. Shukla*,** *S. Seal,* University of Central Florida*; S. Mishra,* University of Memphis

Gold and Silver Sulfide nanoparticles have been successfully synthesized by a novel sol-gel technique. AFM analysis indicates the formation of @<=@12-14 nm and 40-60 nm size Au nanoparticles; while TEM and AFM analysis indicate the formation of Ag@sub 2@S nanoparticles with average size of 26 nm (with broad size distribution ranging from 2.5 nm to 56 nm) and 200-300 nm, for respective H@sub 2@S/not heated and H@sub 2@S/heated samples. XPS analysis of H@sub 2@S/not heated sample, for Au nanoparticles, reveals that the core-level Au 4f@sub 7/2@ B.E. is shifted by +0.3 eV (with increase in the FWHM of 0.2 eV) relative to the bulk value of 84.0 eV. The shift is interpreted in terms of the changes in the electronic structure due to finite cluster size and creation of +ve charge over the surface of cluster during the photoemission process itself. The electronic structure of Au nanoparticles (or clusters) produced via present sol-gel technique is compared with that of Au clusters deposited by evaporation method described in the literature. XPS analysis of Ag@sub 2@S nano and powder particles suggests that the Ag 3d@sub 5/2@ B.E. level is a function of particle size distribution. Moreover, in both the systems, -ve shift in the core-level B.E. is observed, for H@sub 2@S/heated sample, which is attributed to the small size of the particles and their faceted nature. Suitability of the present method to produce silver sulfide ion-selective electrodes is demonstrated by depositing Ag@sub 2@S nanoparticles on the graphite rod and testing its response function.

Organic Films and Devices
Room 313 - Session OF+EL+SS-ThM

Organic Thin Films

8:20am **OF+EL+SS-ThM1 Highly Ordered Layers of Large Conjugated @pi@-systems on Cu(111): A Novel Preparation Method*, G. Beernink*,** *K. Weiss, A. Birkner,* Ruhr-Universität Bochum, Germany*; F. Dötz, K. Müllen,* Max-Planck-Institut für Polymerforschung, Germany*; C. Wöll,* Ruhr-Universität Bochum, Germany

With regard to applications in molecular electronics and the fabrication of nanoelectronic devices, polycyclic aromatic hydrocarbons (PAH), e.g. the graphite segment hexa-peri-hexabenzocoronene (HBC), have recently received considerable attention. For such large PAHs, however, the low solubility in organic or polar solvents and the rather large sublimation temperatures make the application of the commonly used deposition methods, namely adsorption from solution or evaporation in a vacuum system (CVD, OMBE) difficult or even impossible. In this work, we present a direct way to synthesize one particular polycyclic aromatic hydrocarbon, namely hexa-peri-hexabenzocoronene (HBC) by using a surface as a template. A modified precursor molecule, 1,2,3,4,5,6-Hexakis(4-dodecyloxyphen-1-yl)benzene (HPB), which is not planar, is evaporated on a Cu(111) surface. Heating of the substrate leads via thermally induced cyclodehydrogenation to the product HBC, which is characterized by XPS, X-ray absorption spectroscopy (NEXAFS) and STM. The NEXAFS-data directly demonstrate the formation of flat, graphite-like segments which interact only weakly with the substrate, whereas the STM data reveal a high of lateral order.

8:40am **OF+EL+SS-ThM2 The Effect of Conjugation Length on the Frontier Orbital Position of Oligothiophene Derivatives at Metal-organic Interface*, A.J. Makinen*,** *I.G. Hill,* Naval Research Laboratory*; T. Noda, Y. Shirota,* Osaka University, Japan*; Z.H. Kafafi,* Naval Research Laboratory

We report an ultraviolet photoelectron spectroscopy (UPS) study of a novel family of end-substituted oligothiophene derivatives with a varying conjugation length, BMA-nT (n=1-4), where n indicates the number of thiophene rings. These new oligothiophene derivatives are thermally and morphologically stable, and unlike unsubstituted oligothiophenes, which undergo luminescence quenching due to the polycrystalline nature of their solid films, the thiophene derivatives form amorphous films. The BMA-nT compounds show luminescence from the blue (n=1) to the orange (n=4), and additionally they posses hole-transport properties making them attractive materials for organic light-emitting diodes (OLEDs). The UPS results show that the position of the highest occupied molecular orbital (HOMO) of the end-substituted oligothiophenes at the metal-organic interface is dependent on the number of thiophene rings present, i.e. the effective conjugation length of the molecule. We will discuss this property and its implications in the context of carrier injection in an OLED.

9:00am **OF+EL+SS-ThM3 Electronic Properties of @pi@-Conjugated Organic Molecular Semiconductor Interfaces***, A. Kahn,* Princeton University **INVITED**

Metal/organic interfaces are central to a number of organic-based devices. Their electronic structure and chemistry control charge injection. Modeling these interfaces requires an accurate knowledge of the injection barriers, i.e. the position of the transport levels with respect to the metal Fermi level, and of the role of interface chemical reactions. This talk reviews our latest results obtained via direct and inverse photoemission and scanning tunneling spectroscopy on metal interfaces with five organic materials (PTCDA, CuPc, Alq@sub 3@, @alpha@-NPD, @alpha@-6T) of interest for light emitting device and TFT applications. We present the first accurate picture of the transport levels in these materials, levels which are generally unknown because of the strongly correlated nature of molecular solids. The transport gap is found to be significantly larger, i.e. by the exciton binding energy, than the optical gap usually used to describe interface and bulk molecular level diagrams. The exciton binding energy ranges from 0.4eV to 1.4 eV in the materials investigated. Furthermore, we present a detailed and systematic investigation of molecular level alignment at interfaces of organic thin films deposited on a series of metals with different work function. These demonstrate that one of three mechanisms is involved in the formation of the dipole barriers generally observed at such interfaces: (1) lowering of the metal work function by the molecules; (2) electron transfer from the metal to the organics; (3) chemical bonding. Knowledge of the transport gap, interface level alignment mechanisms and interface chemistry leads to a more accurate description of these organic interfaces. Work supported by the MRSEC program of the National Science Foundation (DMR-9809483).

9:40am **OF+EL+SS-ThM5 Effect of Alkyl Substituents on the Adsorption of Thienylenevinylene Oligomers on the Si(100) Surface***, **B. Grandidier**, J.P. Nys, D. Stievenard, C. Krzeminski, C. Delerue,* IEMN/ISEN, France*; P. Blanchard, J. Roncali,* IMMO Universite d'Angers, France

Conjugated thiophene-based oligomers are subject to intense research activity due among others to their potential use as molecular wires in future molecular electronic devices. As microelectronics technology is based on the use of silicon substrates, there is an increasing need to connect these organic molecules to the existing silicon technology. Due to the low intrinsic solubility of the rigid conjugated chains, the synthesis of the longuest chains required the substitution of alkyl chains to the thiophene ring in order to increase the solubility. Whereas such a substitution has limited effect on the electronic structure of the oligomers, it exerts a strong effect on the interactions of the molecules with their physical and chemical environment. The adsorption of unsubstituted and substituted thienylenevinylene oligomers on the Si(100) surface has been investigated using scanning tunneling microscopy. The mode of substitution of the thiophene ring exerts a strong influence on the adsorption configurations and the images of the oligomer based on 3,4-dihexyl thiophene are highly voltage dependent. We discuss the influence of the alkyl chains on the adsorption process and on the appearance of the molecules in the STM images.

10:00am **OF+EL+SS-ThM6 Growth of Films of Thiophene Oligomers by Seeded Supersonic Beams to Improve Control on their Quality and Properties***, **S. Iannotta**, T. Toccoli, A. Boschetti,* CeFSA - Research Center CNR-ITC for the Physics of Aggregates, Italy*; P. Milani,* INFM - Universit@aa a@ di Milano, Italy*; S. Ronchin,* INFM - Universit@aa a@ di Trento, Italy*; A. Podest@aa a@,* INFM - Universit@aa a@ Bicocca, Italy

The growing interest in pi-conjugated organic molecular materials and polymers, driven by wide potential technological impact in electronics and photonics, still faces severe limitations. Applications would be much more favored by improving control on morphology and structure in the solid state. Standard growth methods are based on the self-assembling of the molecules resulting more or less affected by the interaction with the substrate. Very often the resulting films show an inadequate ordering. These problems become severe as the thickness increases over a few monolayers. Fully considering the major role played by the initial state of the molecules at early stages of growth, we approached the problem combining a supersonic free jets that permit to control kinetic energy, momentum and flux with a UHV deposition apparatus. We perform the deposition and simultaneously control the initial state of the seeded organic molecules by varying the parameters of the supersonic expansion (dilution, temperature of the source, form and diameter of nozzle, etc) [P. Milani and S. Iannotta, Synthesis of Nanophase Materials by Cluster Beam Deposition, Springer, Berlin (1999)]. We have prepared a series of films of alpha quaterthiophene that are then characterized by optical measurement, TM-AFM and X-ray diffraction. We report an overall strong evidence of an unprecedented control on morphology, structure and optical response that correlate well to the beam's parameters. PL spectra at low temperature show the vibronic molecular structure very well resolved depending on the initial state of the oligomer in the beam. Films, several hundreds nm thick, show a high degree of ordering with surface morphologies characterized by layered structures of molecular height. X-ray diffraction confirms the high degree of ordering induced by the growth from highly supersonic beams. Correlation between morphology, degree of ordering and the optical response of these films will be discussed.

10:20am **OF+EL+SS-ThM7 Scanning Tunneling Microscopy/Spectroscopy Investigation of the Organic Molecules PTCDA and HBC on Au(100)***, **T. Fritz**, M. Toerker, H. Proehl, F. Sellam, K. Leo,* TU Dresden, Institut fuer Angewandte Photophysik, Germany

Highly ordered organic thin films on gold single crystals have been investigated by Scanning Tunneling Microscopy (STM) and Scanning Tunneling Spectroscopy (STS) at room temperature. The organic dye molecule perylene-tetracarboxylic-dianhydride (PTCDA) has been deposited as submonolayer coverage on Au(100). I-V-spectroscopy at fixed tip-sample-separations has been performed alternately on the PTCDA islands and on uncovered areas of the Au(100) surface. The corresponding normalized derivatives of these I-V-curves have then been compared to inverse photoelectron spectroscopy data known from literature, indicating resonant tunneling via the lowest unoccupied molecular orbital. As a second molecule peri-hexabenzocorone (HBC), also deposited on Au(100), has been investigated. The Au(100) surface has been fully covered by a few monolayers thick, highly ordered HBC film. The normalized derivatives of I-V-curves measured on these films show a pronounced local maximum at a negative voltage of about -1.4 V. By comparison with ultraviolet photoelectron spectroscopy (UPS) measurements of HBC on Au(111) we can show that this peak in the tunneling spectroscopy plot is due to resonant tunneling via the highest occupied molecular orbital of HBC.

10:40am **OF+EL+SS-ThM8 STM, AFM, & Electrochemical Investigations of Squaraine Thin Films***, **M.E. Stawasz**, N. Takeda, B.A. Parkinson,* Colorado State University

Squaraines are a class of organic photoconductors which have found industrial use in photoreceptors of laser printers and xerographic devices, as well as in ablative optical recording material. They have also been investigated for their nonlinear optical characteristics as well as their ability to sensitize large-bandgap semiconductors in photoelectrochemical solar cells. Central to its various uses and characteristics is the squaraine molecules' ability to form organized aggregates, both in solution and in the solid state. Few studies have been done, however, to relate the molecular structure of squaraines to the structure of the aggregates that spontaneously form in thin films. We report STM and AFM data which unambiguously determines thin film/monolayer aggregate structure for a series of hydroxylated and non-hydroxylated dialkylamino-phenyl squaraines with varying alkyl tail lengths deposited on HOPG. Results show that alkyl tail length significantly affects squaraine aggregate structure while the presence or absence of hydroxyl groups does not. Electrochemical investigations of the redox behavior of squaraine thin films using HOPG as the working electrode were also performed. Remarkable redox behavior was observed suggesting a structural change in the squaraine aggregate state upon oxidation. In addition, the effect of electrolyte anion and film thickness on the redox behavior of squaraines was observed, thus providing additional insight into the charge transfer abilities of the squaraine film in the direction normal to the substrate surface.

11:00am **OF+EL+SS-ThM9 Work Function Modification and Surface Chemistry of Indium Tin Oxide with Organosilane Self Assembled Monolayers***, J.A. Chaney,* Naval Research Laboratory*; F. Farzad,* Geo-Centers, Inc. and Naval Research Laboratory*; C.S. Dulcey, R. Shashidar,* ***P.E. Pehrsson,*** Naval Research Laboratory

Attachment of organosilane SAM's with monomers having different dipole magnitude and direction may permit control of the work function (@PHI@) of indium tin oxide (ITO) substrates used in OLED's. However, reliable measurement of @DELTA@@PHI@ requires reproducible control of the environmental conditions. In this work, ITO substrates were treated with SAM's having different head and attachment groups and then inserted into an ultra high vacuum (UHV) chamber. The SAM/ITO work function was measured using an in-vacuo Kelvin probe calibrated with a graphite standard. Surface chemistry was probed by high resolution electron energy loss spectroscopy (HREELS), and electronic structure was investigated by energy loss spectroscopy (ELS). The SAM-modified surfaces usually had lower work functions (@PHI@ = ~4.8-5.3 eV), than bare, oxygen-plasma treated ITO (@PHI@ = ~5.3 eV). The SAM monomers had either one or three Si-OCH@sub 2@CH@sub 3@ units for attachment to the ITO surface. Trifunctional SAM's gave higher @PHI@ values than monofunctional SAM's. The HREELS of monofunctional SAM/ITO showed structure which may be attributable to bending modes. These modes were more intense than on the trifunctional counterpart, possibly due to tighter binding of the latter with ITO. Most SAM modified surfaces showed significant deviation in @PHI@ with time and temperature (up to 200°C), suggesting that adsorption of ambient gasses, even in UHV, affects the SAM/ITO system. However, the work function of some SAM's with hydrophobic head groups was apparently unaffected by adsorption. Differences in the band edge transitions of clean ITO vs. SAM/ITO indicate electronic interactions between the SAM and substrate.

11:20am **OF+EL+SS-ThM10 Effect of Fluoride Layer Insertion on the Electronic Structures of Al/Organic Interfaces@footnote 1@***,* ***Y. Park,*** Korea Research Institute of Standards and Science, Korea*; D. Kim,* Hallym University, Korea*; S. Cho, O. Kwon, G. Lee,* Korea Research Institute of Standards and Science, Korea*; E. Cho,* Chonnam National University, Korea

We have investigated the electronic structures of interfaces between Al and tris-(8-hydroxyquinoline)aluminum (Alq@sub 3@), which is a prototypical organic electroluminescent (EL) material. It has been well known that the insertion of alkali metal fluoride, such as LiF, greatly enhances the EL performance and the origin of such behaviors have been controversial. We used photoelectron spectroscopy techniques including X-ray and UV photoelectron spectroscopy (XPS and UPS) as well as resonant photoemission (RPES) to probe the electronic structure change caused by the insertion of thin layer of various alkaline and alkaline earth metal fluorides between Al and Alq@sub 3@. As previously known, the presence of LiF layer enhanced gap-state formation, but even without the LiF layer, Al deposition significantly alters the electronic structures of Alq@sub 3@. While the insertion of CsF layer showed clear enhancement of the gap states, it was much less obvious for CaF@sub 2@ layer. For both materials, the RPES showed very weak resonant enhancement when excited with photons with the energy near Cs and Ca core level absorption edge. We report similar measurements for various other fluoride materials and discuss their implications. @FootnoteText@ @footnote 1@ This work was supported in part by MOST of Korea through National Research Laboratory Program and Atomic-scale Surface Science Research Center.

11:40am **OF+EL+SS-ThM11 Interface of Aluminum and Poly(vinylidene fluoride with Trifluoroethylene) Copolymer***,* ***B. Xu,*** *C.N. Borca, S. Ducharme, A.V. Sorokin, P.A. Dowben,* University of Nebraska, Lincoln*; V.M. Fridkin, S.P. Palto, N. Petukhova, S.G. Yudin,* Institute of Crystallography, Russia

The interface between aluminum and crystalline copolymer thin films of vinylidene fluoride (70%) with trifluoroethylene (30%) [PVDF-TrFE] has been studied. The ratio of carbon 1s and aluminum 2p core level photoemission peak intensities changes little with increasing emission angle, even after deposition of 5 Å aluminum on the surface of PVDF-TrFE. This indicates that the distribution of aluminum atoms in the copolymer film is quite uniform in the near surface region and that the interface is not abrupt. The contributions to the C 1s core level shift ~1eV to lower binding energy, while the relative ratio of the intensity of C 1s peaks changes, provides further evidence for changes in screening with aluminum doping within the polymer film. The XRD data also shows the crystalline structure of the copolymer film can be deformed with aluminum doping, if the polymer film is annealed.

Plasma Science and Technology
Room 310 - Session PS1+TF+SE-ThM

Fundamentals of Plasma Enhanced Chemical Vapor Deposition

Moderator: A. von Keudell, Max-Planck-Institut für Plasmaphysik

8:20am **PS1+TF+SE-ThM1 Analysis of Pulsed O@sub 2@/TEOS Helicon Plasmas by Time-resolved Optical Spectroscopy***,* ***A. Granier,*** Institut des Materiaux de Nantes, France*; A. Rousseau,* Laboratoire de Physique des Gaz et des Plasmas, France*; L. Le Brizoual,* Institut des Materiaux de Nantes, France

The use of pulsed plasmas instead of continuous plasmas in Plasma Enhanced Chemical Vapor Deposition is known to improve film quality and adherence, due to the reduction of stress. Here, pulsed low pressure (2 mTorr) helicon oxygen/tetraethoxysilane (TEOS) plasmas are investigated by time-resolved optical emission spectroscopy in order to monitor the kinetics and lifetime of radical species in the plasma-off and plasma-on periods. The 300W rf power is 100% modulated and the duty cycle is varied from 1 to 500 Hz. The time behavior of Ar (750 nm), O (844 nm), H (486 nm), OH (306 nm) and CO (296 nm) emissions in the diffusion chamber are studied. The Ar line takes less than 100 microseconds to reach its equilibrium. The H, OH, O and CO intensities take significantly greater times to equilibrate due to the relatively long lifetime of their ground states, and it was necessary to go to a duty cycle of 1 Hz, including a 130 ms plasma-on time and a 860 ms plasma-off time to reach the stationary state. Under the plasma conditions investigated (a 2 mTorr pressure including a TEOS partial pressure of 0.2 mTorr) the OH, O, H intensities take about 1ms, 40ms and 80 ms, respectively to reach their equilibrium. In addition, their intensities normalized to the Argon line intensity increase from a value close to zero at the ignition time, which indicates that the excited states of OH, O, H radicals are created by electron impact excitation on their ground-states and that these radicals have completely disappeared after 860 ms. In contrast, the normalized CO intensity increases from almost zero but has not yet reached its equilibrium after 130 ms, which is consistent with the fact that CO is a stable molecule which is lost by convection to the pump. Additional results obtained in pure oxygen plasmas are also presented and compared to those obtained in O@sub 2@/TEOS plasma.

8:40am **PS1+TF+SE-ThM2 Aluminum Oxide Deposition in an Ionized PVD System***,* ***N. Li***[1]*, D.N. Ruzic,* University of Illinios, Urbana-Champaign*; A. Paranjpe,* CVC Inc.*; J.E. Norman, J.P. Allain,* University of Illinios, Urbana-Champaign

An Aluminum target of a planar magnetron system is powered by a pulsed DC plasma generator to deposit AlOx film using a mixture of Ar and O2. Compared with the conventional sputtering magnetron system, the pulsed directed current (DC) bias is able to discharge the accumulated ions on the insulating AlOx film surface effectively during the positive duty cycle. The chamber also contains a secondary radio-frequency (RF) plasma source to ionize the sputtered metal neutral flux, and generate oxygen atoms and radicals. The directionality of the ion flux can be important for high aspect ratio features. The deposition rates of Al and AlOx films as a function of O2 partial pressure vs. Ar are examined with and without the RF plasma. The deposition rate of AlOx with 400 Watts RF is actually much higher than the deposition rate of Al without the RF at the same total pressure of 25mTorr. Hysterisis curves showing the transition point from metallic mode to poison mode at a certain partial pressure are presented. The presence of a secondary plasma producing ionization makes the metallic sputtering mode possible at a higher O2 partial pressure. A gridded energy analyzer and a quartz crystal microbalance (QCM) are embedded in the substrate plane to allow the ion and neutral deposition rates to be determined. Electron density and electron temperature changes caused by the RF power are measured by a Langmuir Probe. SEM photos of deposited films show differences in film quality as a function of RF power.

9:00am **PS1+TF+SE-ThM3 Surface Transport Kinetics in Plasma Deposition of Hydrogenated Amorphous Silicon***,* ***K.R. Bray,*** *A. Gupta, G.N. Parsons,* North Carolina State University

The concept of dynamic scaling was developed to help understand the role of kinetic phenomena that occur on surfaces during non-equilibrium processes (such as film deposition). Plasma deposition of a-Si:H is particularly intriguing because it is well known that over a wide temperature range, kinetic growth process results in very smooth (non-random) surface texture indicating significant surface species transport, but

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

the growth rate is not thermally activated. We have used rf plasma deposition to form a-Si:H films with both helium and argon diluted silane, and used dimensional and frequency analyses to analyze surface topography obtained from AFM images. Surface fractal scaling parameters, including static (a) and dynamic (b) scaling coefficients, Fourier index, saturation roughness, and lateral correlation length (Lc), were determined as a function of film thickness and temperature. After film coalescence (15-20 s) the scaling coefficients are consistent with the surface topology being described as a self-similar structure: a is constant with growth time and is ~1.0, b is ~4.0, and the saturation roughness value increases exponentially with time as tb/a. Based on Herring's models of surface transport, the scaling coefficient values are consistent with surface smoothening being driven by diffusion. In this picture, the lateral correlation length can be equated with the surface diffusion length. We find that Lc ranges from ~50 to 200nm, and is thermally activated, corresponding to a diffusion activation energy of ~0.2eV. This result has important implications for current growth models, where diffusion length is proposed to decrease with increasing temperature because of increasing density of diffusion-terminating dangling bond sites. Possible modifications to current models, consistent with our observed data, will be discussed and presented.

9:20am **PS1+TF+SE-ThM4 Hydrogenated Amorphous Silicon Fractal Growth and its Relation to the Growth Mechanism***, **A.H.M. Smets,*** Eindhoven University of Technology, The Netherlands*; D.C. Schram,* Eindhoven University of Technology, The Netherlands, Netherlands*; M.C.M. van de Sanden,* Eindhoven University of Technology, The Netherlands

The roughness evolution of the anorphous hydrogenated amorphous silicon (a-Si:H) growth has been studied using in situ HeNe ellipsometry. The a-Si:H depositions are performed using expanding thermal plasma (ETP) deposition technique. With the ETP technique it is possible to grow a-Si:H under dominantly SiH@sub 3@ flux conditions with growth rates ranging over two orders magnitude (1-100 Å/s). The roughness evolution can be divided in an initial growth phase corresponding to a nucleation phase followed by a post initial phase in which the a-Si: H bulk is grown. The post initial growth phase can be described following the universal scaling law, i.e. the roughness scales as t@super beta@ where t is the time and @beta@ the dynamic scaling exponent which depends on the surface relaxation mechanism. The measured scaling exponent @beta@ for growth rates equal or smaller than 22 Å/s is temperature dependent and drops from 0.5 at 100 Celsius down to 0.06 at 500 Celsius. A simple solid on solid (SOS) model is introduced, based upon an activated site at which growth can occur and which can diffuse with a site dependent surface diffusion. With this model the temperature dependent @beta@ can be simulated and the activation energy of the diffusion mechanism can be deduced without the knowledge which process is really responsible for the surface relaxation. The obtained activation energy is equal to ~ 1.0 eV on a terrace site, much higher then what would be expected from physisorbed SiH@sub 3@ dominated a-Si:H growth. At higher growth rates (70 Å/s) the @beta@ shows a maximum around 300 C Celsius. The obtained @beta@ at low temperatures and high deposition rates corresponds to a phase in which the roughness evolution tends more to ballistic fractal growth. Possible relaxation mechanism to explain the high diffusion activation energy will be discussed.

9:40am **PS1+TF+SE-ThM5 Interactions of Chemically Reactive Radicals with Si Growth Surfaces during Plasma Deposition of Si Thin Films***, **S. Sriraman,*** University of California, Santa Barbara, U.S.A*; S. Ramalingam, E.S. Aydil, D. Maroudas,* University of California, Santa Barbara

Hydrogenated amorphous silicon (a-Si:H) thin films grown by plasma deposition from SiH@sub 4@ containing discharges are widely used in photovoltaic and flat-panel display technologies. The structural quality and electronic properties of the deposited films depend on the identities and fluxes of chemically reactive species that originate in the plasma and impinge on the growth surface. Atomic-scale simulations of radical-surface interactions are of utmost importance in understanding the fundamental mechanisms of the deposition process. In this presentation, molecular-dynamics (MD) simulations of radical-surface interactions during deposition of a-Si:H from chemically reactive radicals, SiH and SiH@sub 2@, are analyzed. The simulations reveal a broad class of reaction mechanisms and predict surface reaction probabilities that are in good agreement with experimental measurements. The growth of a-Si:H films starting from an initial H-terminated dimerized Si(001) surface is studied through MD simulations of repeated impingement of the individual radical precursors. Special emphasis is placed on the identification of the elementary surface chemical reactions that govern the deposition process. Effects of the reactions on the growth surface are examined by analyzing local structural configurations and surface chemical reactivity in the vicinity of the surface reaction sites. Evolution of the films' structure, surface morphology and roughness, surface reactivity, and surface composition are analyzed in detail and comparisons made with similar films deposited from individual SiH@sub 3@ precursor. The resulting surface hydride compositions in the deposited films are compared with experimental data. The comparisons are used to discuss our current understanding of the deposition process and implications for plasma deposition of a-Si:H.

10:00am **PS1+TF+SE-ThM6 SiH@sub x@ Radical Densities in a Remote SiH@sub 4@ Plasma for High Rate Deposition of a-Si:H***, **W.M.M. Kessels,** J.P.M. Hoefnagels, M.G.H. Boogaarts,* Eindhoven University of Technology, The Netherlands*; D.C. Schram,* Eindhoven University of Technology, The Netherlands, Netherlands*; M.C.M. van de Sanden,* Eindhoven University of Technology, The Netherlands

The ground state densities of SiH@sub x@ radicals in a remote Ar-H@sub 2@-SiH@sub 4@ plasma used for high rate deposition of device quality a-Si:H (up to 100 Å/s) have been investigated in detail by cavity ring down absorption spectroscopy (CDRS) and threshold ionization mass spectrometry (TIMS). SiH@sub 3@ has been measured by CRDS using the broadband Ã @super 2@A@sub 1@ <- @td X@ @super 2@A@sub 1@ absorption peak at 200 - 260 nm and revealed very good agreement with the TIMS measurements on SiH@sub 3@. SiH@sub 2@ has been measured by TIMS and SiH and Si by CRDS on the transitions A @super 2@@DELTA@ <- X @super 2@@PI@ (~414 nm) and 3p4s <- 3p@super 2@ (~251 nm), respectively. The generation and loss processes for the silane radicals have been investigated thoroughly for different plasma conditions and the contribution of the radicals to film growth has been determined. It is shown that for optimum a-Si:H film properties, the contribution of SiH@sub 3@ is approximately 90%, of SiH@sub 2@ is smaller than 5%, of SiH is ~2%, and of Si is 0.2%. For these conditions, the spatially resolved axial and radial SiH@sub 3@ densities in the plasma are compared with 2-D axisymmetric fluid dynamics model calculations using Phoenics CVD, in which the basic gas phase and surface reactions are taken into account. Furthermore, the first time-resolved silane radical measurements in a modulated rf biased plasma for the determination of the radicals' surface reaction probability will be presented.

10:20am **PS1+TF+SE-ThM7 Fundamentals of Plasma Enhanced Chemical Vapor Deposition***, **J. Meichsner,*** Ernst-Moritz-Arndt-University Greifswald, Germany **INVITED**

Applications of non-isothermal plasmas for chemical vapor deposition and plasma surface modification imply the understanding of the fundamental problem: the plasma-surface interaction. From the plasma physics point of view the transition between the gas plasma and the solid state is characterized by the plasma sheath in front of the surface which controls the flux and kinetic energy of the charged particles. Additionally, in a reactive molecular plasma the complex chemical reactions must be taken into account in the gas phase and at surfaces. Depending on nature of molecular gases, surface material and plasma properties the modification of a thin surface layer, etching or thin film deposition may be found simultaneously on electrodes, immersed samples or surrounding walls. In-situ diagnostic tools are preferably qualified to provide detailed information about processes in the gas plasma and at surfaces. The experimental investigations involved plasma diagnostics by means of optical spectroscopy (OES, LIF) and mass spectrometry (energy selective ion analysis, electron attachment mass spectrometry) as well as surface and thin film characterization using special methods of FTIR-spectroscopy (IRRAS, ATR, fiber based), ellipsometry and microgravimetry. In a low pressure rf-discharge of Hexamethyldisiloxane the chemical conversion of the monomer gas into new stable gas molecules and deposition of a thin organic film were investigated in dependence on characteristic process parameters. The changed atomic composition and molecular structure of the organic films were connected with varied film properties interesting for semipermeable membranes, photo-conducting films, optical or protective coatings. In fluorocarbon plasmas the investigation of the Polyethylene and Polystyrene surface modification as well as thin film deposition revealed the dynamics between incorporation of atoms/molecules and etching of surface material.

11:00am **PS1+TF+SE-ThM9 Thin Film Growth via Surface Reactions of CH@sub 3@, C@sub 2@H@sub 2@ and H as Investigated by Radical Beam Experiments***, M. Meier*[1]*, A. von Keudell,* Max-Planck-Institut für Plasmaphysik, Germany

The knowledge about surface reactions of hydrocarbon radicals is a key element for the understanding of thin film growth in low temperature plasmas using hydrocarbons as precursor gas. Besides the formation of hard coatings by using an additional ion bombardment during growth, it is possible to deposit polycrystalline diamond at elevated substrate temperature from a methane discharge diluted in 99 % hydrogen. The dominant species which are believed to be responsible for diamond formation are atomic hydrogen together with either CH@sub 3@ or C@sub 2@H@sub 2@. In our experiment, we employ particle sources for the production of quantified beams of the radicals CH@sub 3@ and H and for C@sub 2@H@sub 2@ molecules to study the interaction of these species with a hydrocarbon film surface. The emitted fluxes of these beam sources are quantified by using angular resolved ionization threshold mass spectrometry. Recently it has been shown that the sticking coefficient of CH@sub 3@ increases from 10@super -4@ to 10@super -2@ if atomic hydrogen reacts simultaneously with the growing film surface at a low substrate temperature of 320 K. A similar experiment using C@sub 2@H@sub 2@ and H revealed no significant growth via C@sub 2@H@sub 2@ adsorption at the film surface. The variation in the film composition during the synergistic growth is monitored via in situ real time infrared spectroscopy. From the interpretation of these spectra a growth synergism for the simultaneous interaction of CH@sub 3@ and C@sub 2@H radicals with the film surface is observed. This demonstrates that the various synergisms between the growth precursors have to be taken into account for a consistent description of thin film growth via radical adsorption.

11:20am **PS1+TF+SE-ThM10 Deposition Kinetics in Methane rf Glow Discharges: A Combined Experimental and Modeling Study***, **J.R. Doyle**, D. Cole, B. Magocsi,* Macalester College

Methane rf glow discharges are commonly used for diamond-like carbon deposition, but in spite of many experimental and theoretical studies, the details of the plasma chemistry, and in particular the identity of the dominant film precursors, are still debated. In this work we present a comprehensive model of the film deposition using a "semi-empirical" approach. Optical emission measurements and measured electrical properties of the discharge are combined with a Particle-in-Cell/Monte Carlo (PICMC) simulation, which is then used to calculate ion and neutral radical production rates and profiles. Diffusion-reaction-drift (fluid) equations are then solved for stable gas production and ion and radical transport to the electrode surfaces. The model is corroborated by mass spectrometry measurements of the stable gas partial pressures. Film growth rates are calculated from the model and are compared to measured growth rates as a function of pressure and power on both the grounded and powered electrode. The results suggest that C@sub n@H@sub m@ radicals and ions with n > 1 are the dominant sources of mass deposition under conditions used to produce diamond-like films.

11:40am **PS1+TF+SE-ThM11 Using Plasma Energetics to Influence Silicon Nitride Step Coverage***, **K.L. Seaward**,* Agilent Technologies*; M.L. Jezl,* University of Wisconsin, Madison

PECVD silicon nitride is widely used in the fabrication of electronic and optical devices, integrated circuits, and display devices. An important characteristic of PECVD silicon nitride is step coverage, which describes how well the deposition conforms to features that are being coated. Both high and low step coverage are technologically important. In the present work, we investigate altering the plasma energetics to change the amount of PECVD silicon nitride deposited on the underside of structures. Models that predict such step coverage suggest that the precursor sticking coefficient is the dominant factor. Accordingly, different inert gases were added to the deposition plasma to either increase or decrease sticking coefficients by way of increasing or decreasing the plasma electron energy. Depositions were run with 4% ammonia, 1% silane, and 95% He, Ar, Xe, or N@sub 2@. Deposited films were characterized by etch rate, stress, FTIR, Auger, and SEM. Deposition plasmas were characterized by optical emission and rf tuning parameters. The only characteristic related to step coverage was the ratio of N-H bonds to Si-H bonds in the films. Since PECVD silicon nitride films have between 10% and 30% hydrogen content, it is expected that hydrogen plays a large role in film properties. What appears to happen for step coverage is a change in bonding configuration from nitrogen being primarily three-fold coordinated to silicon (high step coverage) to nitrogen being primarily two-fold coordinated to silicon with the third bond being to hydrogen (low step coverage). This latter material, called silicon diimide, is a chemical analog of SiO@sub2@ which, when plasma-deposited with silane, also has low step coverage. This analogy with SiO@sub2@ deposition suggests that precursor sticking coefficients are high during formation of silicon diimide, and this occurred most prominently with mixtures of He and N@sub2@ present in the plasma.

Plasma Science and Technology
Room 311 - Session PS2-ThM

Plasma Diagnostics II

Moderator: E.A. Edelberg, Lam Research Corporation

8:20am **PS2-ThM1 Advanced Actinometry of Inductively Coupled Cl@sub 2@-Ar Plasmas For Plasma Etching***, **N.C.M. Fuller**, I.P. Herman,* Columbia University*; V.M. Donnelly,* Bell Laboratories, Lucent Technologies

The exact composition of Cl@sub 2@-Ar plasmas can influence the overall mechanism and rates of adlayer formation and removal (ion-induced sputtering) during the etching of various materials; therefore, the mixture composition can be altered to improve the overall plasma chemical etching process. To this end, optical emission spectroscopy (OES) and Langmuir probe analysis have been used to measure the electron temperature, T@sub e@ and the absolute species densities in a high-density inductively coupled (ICP) chlorine-argon plasma at 18 mTorr as function of the 13.56 MHz radio frequency (rf) power and argon fraction. In the H (bright) mode, the electron temperature, T@sub e@, measured by trace rare gases optical emission spectroscopy (TRG-OES), increases from 3 eV at 350 W to ~ 6 eV at 770 W for a chlorine plasma (1% Ar). At 600 W (10.6 Wcm@super -2@), T@sub e@ increases from 5.0 eV to ~ 6.5 eV as the argon fraction increases from 0.01 to 0.73. In the E mode at 200 W, the fraction of Cl@sub 2@ that dissociates to form Cl increases from ~10% to ~ 40% as the argon fraction increases from 0.01 to 0.73. In the H mode at 600 W, this dissociation fraction increases from 82% to 96% over the same range. In the H mode and for all argon fractions, the electron density, calculated by a global model, increases by at least an order of magnitude from 300 W to ~ 750 W, and at 600 W it decreases from 1.0 x 10@super 12@ cm@super -3@ to 5.5 x 10@super 10@ cm@super -3@ as the argon fraction increases from 0.01 to 0.73. OES is also used to estimate the peak value of the electron impact excitation cross section for the dissociative excitation of Cl@sub 2@ to the Cl (4p@super 2@ D@super 0@ J@super '@ = 3/2, 5/2) excited state with subsequent emission at 822.2 nm. This peak value is 1.7±0.3 x 10@super -19@ cm@super 2@. The changes in the surface adlayer when the mixture composition is varied will also be discussed.

8:40am **PS2-ThM2 Diagnostics of Inductively Coupled Chlorine Plasmas: Measurements of the Neutral Gas Temperature***, **V.M. Donnelly**, M.V. Malyshev,* Bell Laboratories, Lucent Technologies

We report measurements of the bulk, neutral gas temperature in a chlorine inductively coupled (ICP), or transformer-coupled plasma (TCP). A trace amount (2-5%) of N@sub 2@ was added to the discharge and the rotational temperature of the C-state was determined from the C->B emission in the ultraviolet. This temperature has been shown by others to be equal the rotational temperature of ground state N@sub 2@, which is the thermally equilibrated (translational and rotational) gas temperature (T@sub g@). The gas temperature 3 cm above the wafer is equal to, or only slightly above the wall temperature (300 K) throughout the low-power, capacitively-coupled regime (

9:00am **PS2-ThM3 A New Diagnostic Method for Monitoring Plasma Reactor Walls: Multiple Total Internal Reflection Infrared Surface Probe***, **A.R. Godfrey**, S.J. Ullal, E.S. Aydil,* University of California, Santa Barbara*; E.A. Edelberg, L.B. Braly, V. Vahedi,* Lam Research Corporation

One of the major concerns in plasma etching of thin films with high density inductively coupled plasma (ICP) reactors is wafer-to-wafer etch rate reproducibility. Inductively coupled plasma reactors are typically operated at low pressures where the mean free path of species in the plasma is on the order of the reactor dimensions. As a result, reactive radicals collide with the chamber walls as often as they do with each other in the gas phase and the walls play a crucial role in determining the plasma properties and etching behavior. Thus, it is critical to monitor the wall conditions and the nature of the films and adsorbates that are deposited on the walls. We have developed a surface probe based on in situ multiple total internal reflection Fourier transform infrared (MTIR-FTIR) spectroscopy that can be used as a diagnostic technique to monitor the films and adsorbates on the

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

walls of both plasma etching and deposition reactors. A small (5 cm x 1 cm x 0.1 cm) trapezoidal shaped infrared transparent crystal with 45° beveled edges is placed flush with the reactor walls with the beveled edges facing small IR transparent windows. Infrared beam from a spectrometer is focused onto one of the beveled edges and made to undergo multiple total internal reflection through the crystal before exiting it from the opposite beveled edge. The films deposited on the crystal surface are sampled by the infrared beam which is collected and detected using an IR detector. This diagnostic method enables in situ monitoring of the deposits on the reactor walls during plasma processing. The MTIR-FTIR surface probe and its applications to monitoring reactor walls during plasma etching and deposition processes will be described in detail. Specifically, this talk with emphasize application of the MTIR-FTIR probe to monitoring the walls of a Lam ICP reactor during etching of Si with Cl@sub 2@/O@sub 2@ gases and subsequent cleaning in between etched wafers with a F containing discharge.

9:20am **PS2-ThM4 Laser-Aided Diagnostics of Discharge Plasmas***, **K. Muraoka**, K. Uchino, M. Bowden, M. Maeda,* Kyushu University, Japan **INVITED**

In order to understand, and ultimately optimize discharge plasmas for various purposes, we have to know spatio-temporal distributions of (1) electric fields, (2) electron density and temperature (or EEDF itself if it is away from Maxwellian), and (3) reaction products. The authors have extensively explored potentials of laser-aided plasma diagnostics (LAPD) for this purpose and applied it to various discharges. These are developments and applications of laser optogalvanic spectroscopy (LOG) and laser-induced fluorescence (LIF) to detect Stark effect for (1), Thomson scattering to measure electron density and temperature/EEDF for (2), and LIF, Raman scattering, Rayleigh scattering, and ultra-violet absorption to measure density and temperature of atoms and molecules for (3). Each of these is described, with a special emphasis being placed on (2).

10:00am **PS2-ThM6 Energy Distributions of Incident Ions to a RF-Biased Substratep***, **H. Kawada**, N. Tsumaki,* Hitachi Ltd., Japan

Energy distributions of incident ions and molecules to a substrate exposed to a plasma generated in fluorocarbon gas was obtained by a Quadrupole Mass Spectrometer equipped with an energy filter which was operated with time modulation. The incident ions a nd molecules which entered into an orifice opened in the substrate surface were analyzed by the QMS mounted under the orifice. An 800-kHz radio frequency (rf) voltage was applied to the substrate, as it is commonly done in order to enhance dry etching rea ction on wafers mounted on the substrate. Because of the alternating voltage in the rf, an electrical potential of the substrate is also alternating and not constant. On the other hand, the reference potential used for the QMS optics is not always equal t o the potential of the substrate because the QMS optics must be electrically insulated and kept stable for normal operation. Therefore, post-acceleration of the ions would occur by the unstable potential difference between the substrate and the QMS optics, after the incident ions has received kinetic energy in acceleration between the plasma and the substrate. Such the post-acceleration causes a large error in measuring the kinetic energy that is essential of the incident energy. In order to obtain real energy distributions by minimizing the post-acceleration, time modulation was carried out in our detection setup, that is, the incident energy was measured only at the moment when the rf voltage of the substrate was equal to the reference potential in the QMS optics. Furthermore, by varying the reference potential, the incident energy could be measured at a specific phase of the rf voltage of the substrate. We also measured relative densities of radicals caused in the plasma by using Infrared Laser Absorption Spectroscopy. The energy distributions of the incident ions at a specific bias phase, and its correlation to the radical densities will be shown and discussed.

10:20am **PS2-ThM7 Energy and Angular Distribution of Ions Effusing from a Hole in Contact with a High Density Plasma***, **D. Kim**, C.-K. Kim, D.J. Economou,* University of Houston

The energy and angular distribution of ions extracted from a hole in contact with a low- temperature plasma have been investigated both computationally and experimentally. A single hole is thought to be a well-defined system for understanding the interaction of a plasma with a biased grid. Such plasma-grid interaction finds applications in neutral beam etching, ion sources, satellite thrusters, etc. The plasma parameters (Debye length), hole diameter and thickness determine the characteristics of the ions (and fast neutrals) extracted through the hole. We have developed a Monte Carlo simulation to follow the trajectories of ions and fast neutrals from the bulk plasma through the sheath and out the hole. Collisions with gas phase species and the walls of the hole are taken into account. We have also measured the energy and angular distribution of ions effusing from a hole on a wall in contact with a high density plasma. A hemispherical sectioned electrode is used as the detector. The hole diameter is varied from 25 to 1000 microns and the hole aspect ratio (depth to diameter) is varied from 0.25 to 10. The energy and angular distributions in both experimental data and simulations reflect the strong disturbance of the sheath when the hole size exceeds the local Debye length.

10:40am **PS2-ThM8 Electron Temperature and Ion Energy Measurements with A High-resolution, Sub-micron, Retarding Field Analyzer***, **M.J. Sowa**, M.G. Blain, R.L. Jarecki, J.E. Stevens,* Sandia National Laboratories

A silicon wafer-based, submicron, high-resolution, retarding field analyzer (RFA)@footnote 1@ was used to measure ion energy and infer electron temperature (Te) in an inductively coupled plasma. RFA ion energy measurements are expected to have a resolution of < 0.1 eV based on simulations. By monitoring the flux of ions to the collector of the RFA while allowing the shield to float, we are able to measure the local difference between the plasma and floating potentials. From this difference, the electron temperature can be calculated directly from sheath theory. Experimental conditions include 10, 20, and 40 mTorr Ar at 100, 200, and 300 W of plasma source power at axial positions of 42-217 mm from the source dielectric window. RFA Te values were compared to those obtained with single and double probes. Excellent agreement was observed between the single probe and RFA over all conditions. Double probe measurements matched the other measurement techniques at 20 and 40 mTorr, and gave 5-30% higher Te values at 10 mTorr. The ion energy spreads measured with the RFA are close to Gaussian with standard deviations from 1.8-2.2 eV. The ion energy spread increased weakly with pressure but showed little dependence on the position or the measured Te value, which ranged from 1.3 - 2.7 eV.@footnote 2@ @FootnoteText@ @footnote 1@ M.G. Blain, J.E. Stevens, J.R. Woodworth, Appl. Phys. Lett., v.75, n.25, p.3923, 1999. @footnote 2@ Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under contract DE-AC04-94AL85000.

11:00am **PS2-ThM9 Mass Resolved Ion Energy Distribution Measurements in an Inductively Coupled H@sub 2@/Ar Plasma with a Highly Collisional Presheath***, **S. Agarwal**, D. Maroudas, E.S. Aydil,* University of California, Santa Barbara

Ion energy distributions (IEDs) in a plasma are determined by the spatio-temporal variation of the potential in the sheath and the presheath. In practice, it is not possible to directly measure the electric field in these regions as they are very thin and easily perturbed by a probe. However, in cases were the preseheath/sheath is collisional and/or the transit time through the sheath is comparable to the rf cycle, structured ion energy distributions are obtained which may be used to compute the electric field in the plasma near a surface. Mass-resolved IED measurements were made using a QMS equipped with a Bessel box energy analyzer in a H2/Ar plasma. The ions were sampled through an aperture on the grounded electrode in a helical resonator plasma reactor through a 2.8 degrees solid angle to detect mostly those ions that have been created by inelastic collisions. These ions preserve information about the electric fields in the sheath and the presheath. The ionic species detected were H+, H2+, H3+, Ar+, and ArH+. The IEDs for H+, H2+ and H3+ showed multiple peaks (as many as 20) superimposed on a saddle structure whereas the IEDs for Ar+ and ArH+ showed only a single peak approximately centered at the time averaged plasma potential. The saddle shaped IED arises because the transit time through the sheath for the lighter ions is less than the rf cycle and the multiple peaks arise due to charge exchange or proton transfer reactions or electron impact ionization in the quasi-neutral presheath region. If there are collisions in the sheath, the peaks appear at an energy lower than the saddle shaped curve. However, in the present measurements, the peaks were superimposed on the saddle curve itself, which means that they arise from collisions in the presheath and subsequent splitting of this multi-peaked distribution in the thin collisionless sheath region. The number and position of the peaks can be used in principle to reconstruct the electric field in the plasma.

11:20am **PS2-ThM10 Langmuir Probe Analysis for High Density Plasmas***, **F.F. Chen**,* University of California, Los Angeles

The theory of Langmuir probes has been reexamined for use in high-density plasma tools with plasmas in the N = 10@super 11-13@ cm@super -3@ range. The most accurate computations for collisionless plasmas have been done by Laframboise,@footnote 1@ but the results are difficult to apply to data because of the normalized units used. Up to now, for densities in the 10@super 9-11@ cm@-3@ range, the simpler Orbital Motion Limited (OML) theory has sufficed. The two theories agree at low densities. To make the Laframboise curves accessible for real-time I - V analysis of probe data at higher N, we have found analytic approximations to the curves by a double parametrization technique. Furthermore, an iterative procedure permits separating the ion and electron currents in their overlap region, thus yielding an accurate fit to the shape of the ion characteristic and hence accurate values of N and KT@sub e@ regardless of the density range. Comparison with experiment, however, gives surprising results. For N such that the ratio of probe radius to Debye length exceeds 3 (thin sheaths), the OML theory is expected to fail, but it fits the SHAPE of the ion characteristics better than the Laframboise theory, which gives N values 2-3 times higher. The latter seems to agree better with independent measurements of N using microwaves or plasma oscillation probes. We have also parametrized an intermediate theory, that of Allen, Boyd, and Reynolds,@footnote 2@ but this gives unreasonably low N values. A possible cause of the paradox is the effect of charge-exchange collisions. @FootnoteText@ @Footnote 1@ Laframboise, J.G., Univ. Toronto Inst. Aerospace Studies Rept. 100 (June, 1966). @Footnote 2@ Allen, J.E., Boyd, R.L.F., and Reynolds, P., Proc. Phys. Soc. (London) B70, 297 (1957).

11:40am **PS2-ThM11 Single Photon Ionization as a Probe of Radicals in Hot-Wire and Plasma Processing**, *H.L. Duan, **S.F. Bent,*** Stanford University

Gas phase radicals produced in both plasma and hot-wire sources for etching or deposition can influence reaction pathways, reaction rates, and product distributions. Identifying and monitoring the concentrations of free radicals during processing is generally difficult due to the short radical lifetime and low radical concentrations relative to the background. Here we describe the use of a single-photon vacuum ultraviolet (VUV) photoionization technique for the detection of free radicals during thin film growth. In this technique, VUV radiation at 118 nm is generated by frequency mixing of the output of a pulsed Nd:YAG laser to obtain the ninth harmonic. Photons at 10.5 eV contain sufficient energy to ionize many radicals of interest; the laser-ionized ra dicals are then detected by time of flight mass spectrometry. The potential of SPI as a radical probe in electronic materials processing will be demonstrated in studies of two chemical vapor deposition systems using hot-wire activation (HW-CVD): growth o f amorphous hydrogenated silicon (a-Si:H) thin films using silane and growth of amorphous silicon carbon alloys from methylsilane precursor gases. The SPI probe allows for simultaneous detection of Si, SiH@sub x@, Si@sub 2@H@sub y@, and CH@sub 3@ radicals present in the gas phase. It is shown that, other than H atoms, Si atoms are the dominant radicals produced by the hot tungsten filament in the presence of silane. Hydrogen dilution is found to change the gas phase silyl radical distribution. In the case of methylsilane decomposition on the hot wire, methyl radicals are produced in addition to Si-containing radicals. Studies as a function of filament temperature, filament aging, and hydrogen dilution demonstrate the strength of this technique for monitoring reactive radicals in situ with both spatial and temporal resolution. The use of the SPI method for radical detection in plasma processing will also be discussed.

Semiconductors
Room 306 - Session SC+EL+SS-ThM
Hydrogen On and In Semiconductors

Moderator: J.T. Yates, Jr., University of Pittsburgh

8:20am **SC+EL+SS-ThM1 Step Structures and Energies on Vicinal Si(001) Monohydride Surfaces: Dependence on H Chemical Potential**, ***A. Laracuente**, L.J. Whitman,* Naval Research Laboratory

It is well known that foreign adsorbates can alter the equilibrium step structure on surfaces and often have a dramatic effect on film growth. Given that most semiconductor devices are fabricated in hydrogen-rich environments on silicon substrates, a comprehensive understanding of how hydrogen affects Si step energies is essential to the development of accurate models of semiconductor growth and processing. We have determined the equilibrium step structures and step formation energies for the whole range of monohydride-terminated (001)-terrace-plus-step surfaces. Compared with the clean surfaces, hydrogen termination alters the atomic-scale step edge structure and, in many cases, causes large-scale changes in the surface morphology. The structural modifications result directly from a change in the relative energies of the possible single- and double-layer step configurations. On nominal Si(001), the S@sub B@ steps are mostly non-rebonded and rougher after H passivation. A kink distribution analysis reveals that H reduces the nearest neighbor interaction across the S@sub B@ steps by an order of magnitude. Whereas the nearest neighbor interaction strongly depends on H@sub 2@ pressure, i.e. the H chemical potential, the step formation energies do not. On D@sub B@-stepped surfaces, such as Si(1 1 11), a statistical analysis of the steps shows that H lowers the formation energy of non-rebonded D@sub B@ and S@sub B@ steps, making them close in energy to the rebonded D@sub B@ steps. Post annealing a monohydride Si(1 1 11) surface without H significantly changes the n-D@sub B@/r-D@sub B@ ratio, indicating that the D@sub B@ step formation energies strongly depend on H chemical potential.

8:40am **SC+EL+SS-ThM2 Si(100) Surface Roughening and H Atom Absorption: Surface and Bulk Characterizations.**, ***S.K. Jo**, J.H. Kang,* Kyung Won University, S. Korea*; X. Yan, J.M. White, J.G. Ekerdt,* University of Texas at Austin*; J. Lee,* Seoul National University, S. Korea*; J.Y. Maeng, S.H. Kim,* Korea Advanced Institute of Science and Technology

Absorption of thermal-energy gaseous hydrogen atoms by Si(100), exceeding by far the dopant and other impurity concentrations, occurs within a narrow substrate temperature (T@sub s@) window centered at ~ 460 K. The absorbed hydrogen persists in the crystalline bulk as highly mobile species before migrating out and desorbing as molecular hydrogen at T@sub s@ as high as 900 K, well above the recombinative desorption temperatures of surface-adsorbed H. Developing and sustaining atomic-scale surface roughness, by H-induced silicon etching, is a prerequisite for H absorption and determines the T@sub s@ window. In support of these conclusions are our TPD, Raman, SIMS, TEM, and STM data for this fundamental and interesting phenomenon of thermal H atom absorption by Si(100).

9:00am **SC+EL+SS-ThM3 Dissociation Pathways of Molecular Hydrogen on Silicon Surfaces@footnote 1@**, ***U. Höfer,*** Philipps Universität Marburg, Germany **INVITED**

The dissociative adsorption of H@sub 2@ on Si(001) has emerged as a prototype for activated chemical reactions on semiconductor surfaces. One of the most distinctive features of this basic reaction is the low sticking probability for dissociative adsorption (< 10@super -11@) and the fact that thermally induced distortions of the Si lattice enhance the reactivity by many orders of magnitude. In order to reveal the atomic-scale motion responsible for "phonon assisted sticking" we have performed a series of experiments employing optical second-harmonic generation (SHG), supersonic molecular beam dosing, and scanning tunnelling microscopy (STM). It will be demonstrated that, similar to thermally activated dynamical distortions, the reactivity can be enhanced by static distortions of the surface by precoverage with atomic hydrogen or by steps. The barriers to adsorption at these well-defined sites were determined. They revealed systematic trends that could be reproduced by density functional calculations and traced back to the interplay between electronic structure and local distortions of the Si surface. We find that hydrogen adsorption proceeds via inter-dimer reaction pathways in all cases. Whenever the energy splitting between the reactive dangling-bond states of adjacent dimers may be reduced by low-energy displacements of Si atoms, the adsorption barrier is found to be low. @FootnoteText@ @footnote 1@ Work performed in collaboration with W. Brenig, A. Biedermann, M. Dürr, T. F. Heinz, M. Hilf, Z. Hu, P. Kratzer, E. Pehlke, M. B. Raschke and M. Scheffler.

9:40am **SC+EL+SS-ThM5 Hydrogen Bonding on Compound Semiconductor Surfaces**, ***R.F. Hicks**, Q. Fu,* University of California, Los Angeles*; L. Li,* University of Wisconsin, Milwaukee*; C.H. Li,* University of California, Los Angeles

Hydrogen adsorption on gallium arsenide and indium phosphide (001) surfaces has been studied by scanning-tunneling microscopy and internal-reflection infrared spectroscopy combined with ab initio molecular cluster calculations. The calculations are based on a series of clusters that accurately simulate the group III and V dimer termination of the surface. Good agreement has been achieved between the vibrational frequencies predicted by the theory and those observed in the experiments. On the anion-rich surfaces, hydrogen adsorbs on arsenic (or phosphorous) dimers to form isolated and coupled monohydrogen bonds and dihydrogen bonds. Conversely, on the cation-rich surface, hydrogen adsorbs on gallium (or indium) dimers to form terminal and bridged metal hydrides. The latter species occur in isolated or coupled structures involving two or three metal atoms. The implications of these results for the surface science of compound semiconductors will be discussed at the meeting.

10:00am **SC+EL+SS-ThM6 Scanning Tunneling Microscopy of Low Temperature Adsorption H2 on GaAs(001)**, ***H. Xu,*** National University of Singapore, Singapore*; Y. Lee, J. Lee, A. Lee,* National University of Singapore

The variable temperature scanning tunneling microscope (VT-STM) has been used to study in-situ the transition of 2x6 reconstruction of GaAs (001) at low temperature. High resolution STM images show that the metastable As dimers rows of 2x6 reconstruction in GaAs (001) becomes unstable under the attack of the dissociated adsorption H@sub2@. As dimers were broken firstly due to the formation of double atom lines structure by the attacking of hydrogen on As dimers atoms. Furthermore, the opened As atoms rows on the top of this surface were twisted gradually up to coalesce together with a width of 3 As dimers. Unexpectedly, these compressed As atoms suddenly extend along the original As dimers rows direction(-110) gives rise to form a metastable trimer As rows.

10:20am **SC+EL+SS-ThM7 Theoretical Approaches for Predicting SiGe Heteroepitaxy**, ***C. Mui****, S.F. Bent, C.B. Musgrave,* Stanford University

The demand for silicon-germanium devices has been growing in recent years due to potential applications in areas such as infrared photodetection, wireless communications and quantum nanostructures. The need for improved SiGe processing has motivated efforts to better understand the detailed reaction mechanisms of SiGe heteroepitaxy, including the adsorption of gas phase precursors and the removal of hydrogen from SiGe surfaces. We have used Becke3LYP density functional theory to study the effect of Ge alloying on the energetics and kinetics of H2 desorption from SiGe surfaces. We have investigated H2 desorption from the Si-Si homodimer, the Si-Ge heterodimer and the Ge-Ge homodimer sites. We found that in the transition state the two desorbing hydrogen atoms are localized above one surface atom, such that the structure resembles a dihydride species. The transition states on all three types of dimers have similar geometries, independent of the identity of the surface dimer atoms. Furthermore, the activation barriers depend only on the identity of the dimer atom not bonded to the desorbing hydrogens. For example, the activation barrier for H2 desorption from the Si site of a Si-Ge heterodimer is lower than that from a Si-Si homodimer by 10.6 kcal/mol. However, the barrier for desorption from the Ge-Ge homodimer is the same as that from the Si site of a Si-Ge heterodimer. We also found that the activation barrier for H2 desorption is only affected by surface Ge, and not Ge in the bulk. Calculations on a three dimer cluster showed that the activation barriers are dependent on cluster size, indicating that charge transfer and surface strain play a role in the desorption process. Finally, we will present results concerning additional surface reactions including the adsorption of germane on SiGe surface dimers.

10:40am **SC+EL+SS-ThM8 Real-time Monitoring of H@sub 2@ Adsorption on C(001) at High Temperature by Ultraviolet Photoelectron Spectroscopy**, ***Y. Takakuwa****, M. Asano,* Tohoku University, Japan

The hydrogen-terminated diamond surface has attracted much attention not only as a high efficiency electron emitter because of its electron affinity being negative (NEA) but also as a p-type conductive surface for field-effect-transistor devices. On the other hand, H@sub 2@ desorption on the hydrogen-terminated diamond surface occurs appreciably at higher temperature than 900@super o@C. This suggests that during the synthesis of diamond thin films by chemical vapor deposition using hydrocarbon gases such as methane the diamond-growing surface could be terminated by hydrogen and therefore NEA, even though the growth temperature is as high as 800-1000@super o@C. In this study, the electron affinity, secondary electron emission and pinning position of the Fermi level during exposing a diamond C(001) surface to H@sub 2@ at 700@super o@C and 1x10@super -5@ Torr were investigated by a real-time monitoring method of ultraviolet photoelectron spectroscopy. It was observed that (1) molecular hydrogen not activated by a hot tungsten filament absorbs dissociatively on the C(001) surface, wile it takes about 120 min to cover wholly the surface with hydrogen; (2) the electron affinity decreases from +0.4 eV for the clean surface to a negative value when the hydrogen coverage is about 90%; (3) the Fermi level is positioned at 0.61 eV above the valence band maximum just when the diamond surface changes to NEA; (4) the secondary electron yield increase with the hydrogen exposure time even after the complete termination of the surface with hydrogen. On the basis of the observed results, the time evolution of the surface electronic state during the hydrogen adsorption on the C(001) surface is discussed.

11:00am **SC+EL+SS-ThM9 Infrared Studies of Hydrogen on Diamond (100)**, ***J.N. Russell, Jr.,*** Naval Research Laboratory*; J. Hovis, R.J. Hamers,* University of Wisconsin*; G.T. Wang, S.F. Bent,* Stanford University*; M.P. D'Evelyn,* General Electric CRD*; J.E. Butler,* Naval Research Laboratory

Hydrogen atoms play a critical role in the chemical vapor deposition of diamond thin films. Currently, hydrogen plasmas are used to produce reproducible, clean, smooth, diamond (100) single-crystal surfaces. The use of diamond films for microelectronic or surface acoustic wave devices requires a fundamental understanding of the diamond surface termination and its interaction with adsorbed species. The hydrogen terminated diamond (100) surface is comprised of two 2x1 domains of monohydride surface dimers. Using s- and p-polarized multiple internal reflection infrared spectroscopy, the symmetric and asymmetric stretches of the HCCH surface dimer are easily resolved and are compared to ab initio calculations of the frequencies. The thermal dependence of the CH stretches is monitored as a function of the anneal temperature. When the hydrogen terminated surface is covered with a condensed layer of physisorbed molecules, the surface CH vibrational frequency is significantly influenced. We discuss the implications of these observations.

11:20am **SC+EL+SS-ThM10 Fundamental Connection Between the ESD of H/D at Silicon Surfaces and at Oxide/Silicon Interfaces**, ***K. Cheng****, J. Lee, Z. Chen, J.-P. Leburton, E. Rosenbaum, K. Hess, J.W. Lyding,* University of Illinois, Urbana-Champaign

Parallels can be drawn between electron stimulated desorption (ESD) of hydrogen at silicon surfaces in UHV and the ESD of hydrogen at the oxide/silicon interface in CMOS transistors. In particular, the multiple carrier vibrational heating mechanism for ESD, and the giant hydrogen/deuterium isotope effect play important roles in interface degradation. In this paper we will present results demonstrating the primary role of channel hot carriers in the degradation of the oxide/silicon interface of transistors. Experiments performed on p-channel MOSFET's show essentially no isotope effect for the creation of interface traps when carriers are injected into the oxide. However, a large isotope effect, consistent with vibrational heating, is observed when carriers flow along the oxide/silicon interface. One key difference between a H-passivated silicon surface and a H-passivated oxide/silicon interface is that there is a distribution of Si-H bond strengths at the interface due to variations in the amorphous oxide matrix. Experimental results will be presented which directly measure this distribution as well as show its ramifications in terms of rapid interface trap creation. The significance of this study comes from the fact that it is still a widely held view that the dominant transistor degradation mechanisms arise from carrier injection into the oxide, and therefore will be scaled away as industry trends progress. However, by performing new experiments and using basic surface science as a setting for their interpretation, we are able to show that there are fundamental problems with this view. Our results are supported by the fact that even state-of-the-art 0.18mm, 1.5 V CMOS chips show hundreds times lifetime improvement when hydrogen is substituted by deuterium.

11:40am **SC+EL+SS-ThM11 Depth-Resolved Determination of the Hydrogen Concentration at Buried SiO@sub 2@/Si(100) Interfaces by Resonant Nuclear Reaction Analysis**, ***M. Wilde****, M. Matsumoto, K. Fukutani,* University of Tokyo, Japan*; Z. Liu, Y. Kawashima,* NEC Corp., Japan

Hydrogen at the SiO@sub 2@/Si interface has been discussed to affect the electronic performance of MOS diodes by influencing the density of states at the interface. Drastic improvements of the reverse current resistance were reported after H@sub 2@-annealing of such devices.@footnote 1@ In this study the hydrogen concentration at the SiO@sub 2@/Si interface is measured directly by a Nuclear Reaction Analysis (NRA, based on the @sup 1@H(@sup 15@N, @alpha@@gamma@)@sup 12@C reaction), and the influence of H@sub 2@-annealing is investigated. Oxidized Si(100) samples with SiO@sub 2@ films of (19.0 - 41.5 nm) thickness were studied. In the as-oxidized condition, H near the SiO@sub 2@/Si interface is identified at a concentration lower than 4x10@sup 19@ cm@sup -3@. In the NRA depth profiles of all samples the center of the near-interface H-distribution appears at a depth (5±1) nm shallower than the interface location determined by ellipsometry. While no H is found in the silicon substrate, hydrogen is accumulated in a several nm wide layer within the oxide film adjacent to the interface. This result supports the idea of a transition region between the mere interface and the SiO@sub 2@ material, where stoichiometry and strain-induced defects may act as local bonding sites for hydrogen. In-situ annealing of the oxidized wafers in ambient H@sub 2@ gas causes a substantial increase of the H-concentration near the SiO@sub 2@/Si(100) interface, whereas the width of the H-distribution and its position within the oxide film remain unchanged. The H-distribution is thermally stable below the annealing temperature of 400@deg@C. On heating to higher temperatures in vacuum depletion of H from the interface layer occurs to a concentration level below the as-oxidized condition. Hydrogen can be replenished at the interface by repeating the H@sub 2@-annealing procedure. @FootnoteText@ @footnote 1@ S. Fujieda, H. Nobusawa, M. Hamada, T. Tanigawa, J. Appl. Phys. 84 (1998) 2732.

Surface Science
Room 208 - Session SS1+MC-ThM
Oxide Applications and Oxidation

Moderator: E.I. Altman, Yale University

8:20am **SS1+MC-ThM1 Synthesis and Characterization of Self-assembled Cu@sub2@O Quantum Dots on SrTiO@sub3@(001) Surface***, **Y. Liang**, D.E. McCready, A.S. Lea, S.A. Chambers, S. Gan,* Pacific Northwest National Laboratory

Self-assembled quantum dots have received much attention recently because their atom-like electronic and optical behavior can be tailored. One common problem with many quantum dots has been the poor chemical and thermal stability as most of them are made of conventional semiconductors. An alternative to this problem is to use oxide based quantum dots due to their superior stability. We have successfully synthesized self-assembled Cu@sub2@O quantum dots on SrTiO@sub3@ substrates using a molecular beam epitaxial method. The structure and chemical states of Cu@sub2@O quantum dots have been confirmed by x-ray diffraction and x-ray photoelectron spectroscopy (XPS). Reflection high energy electron diffraction (RHEED), atomic force mic roscopy (AFM), and high-resolution scanning Auger microscopy (SAM) show that formation of Cu@sub2@O quantum dots occurs after deposition of a few monolayers of Cu@sub2@O due to the large compressive lattice mismatches between Cu@sub2@O and SrTiO@sub3@. SAM reveals that the interdiffusion between Cu@sub2@O quantum dots and SrTiO@sub3@ is significantly less than many other quantum-dot systems. XPS further shows that the interfacial electronic structure of Cu@sub2@O/SrTiO@sub3@ exhibits the so-called the type-II heterojunction, i.e., the valance and conduction bands of Cu@sub2@O are both higher than that of SrTiO@sub3@. Consequently the photo-excited electrons and holes are spatially separated with holes being confined to Cu@sub2@O quantum dots and electrons confined to SrTiO@sub3@, a property important for photocatalysis and solar cell applications. We are currently using AFM-based surface potential measurements to elucidate the spatial charge separation behavior of this system upon photo-excitation at different wavelengths. @FootnoteText@ # Pacific Northwest Laboratory is a multiprogram national laboratory operated by Battelle Memorial Institute for the U.S. Department of Energy under Contract DE-AC06-76RLO 1830.

8:40am **SS1+MC-ThM2 Correlation of Electronic Structure with Photoluminescence Properties in Oxidized Silicon Nanoclusters***, **J.A. Carlisle**, I. Germanenko, Y. Pithawalla, M.S. El-Shall,* Virginia Commonwealth University

The relationship between morphology, band-gap size, and photoluminescence data in surface-oxidized silicon nanoclusters is established using photon-yield measurements at the Advanced Light Source. After removal from the growth chamber, photoluminescence (PL) results indicate that as the clusters oxidize, the main PL peak moves from 1.83 eV to 1.94 eV in energy. The central focus of this work is to establish the origin of the PL peak, whether it arises due to quantum size effects or due to the formation of suboxides as the clusters oxidize. The changes in the morphology and bonding structure of the clusters were established using soft-x-ray fluorescence spectroscopy (SXF) and photon-yield near-edge x-ray absorption fine structure (NEXAFS) spectroscopy, which probe the element-specific density of occupied (SXF) and unoccupied (NEXAFS) electronic structure. Our finding is that the as-synthesized nanoclusters consist of a pure, crystalline Si core within a nearly pure SiO2 shell. Very few suboxides are present, and the oxidation process does not lead to an increase in the amount of suboxides present within the particles. As the nanoclusters oxidize, the radius of the crystalline core decreases in size, which gives rise to the change in the position of the PL signal.

9:00am **SS1+MC-ThM3 The Behavior of Ultrathin Al@sub 2@O@sub 3@ Films in Very High Electric Fields: STM-induced Pitting and Dielectric Breakdown***, N.P. Magtoto, C. Niu, **J.A. Kelber**,* University of North Texas

The behavior of ultrathin oxides under high electric fields is of critical importance to areas as diverse as microelectronics (gate oxides, magnetoresistance devices) and corrosion. We report the use of high electric fields applied via the STM to induce pits and dielectric breakdown in ultrathin @gamma@'-Al@sub 2@O@sub 3@ films (7 Å thick) grown on Ni@sub 3@Al(111) substrates in UHV. Voltage pulses (bias voltages of 1-6 V, either polarity) are applied to a specific location on the oxide surface with the feedback current loop operative to prevent tip/sample physical interaction. Subsequent imaging at 0.1 V bias voltage and 1 nA feedback current reveal the effects of high field on surface composition and topography. Results show that dielectric breakdown occurs at a field of 12.3±0.7 MV/cm. Breakdown is marked by the creation of an area ~20 nm high and 100 nm wide and the loss of the insulating nature of the oxide as deduced from I/V spectroscopy. Once the threshold breakdown voltage is reached, the STM tip retracts precipitously (~20-25nm) from the sample surface due to the onset of the leakage current. At fields ~ 60 % of breakdown, small pits in the oxide that are 0.4-0.8 nm deep can be created. Repeated application of this field within the pit will cause dielectric breakdown, even though the same field will not induce breakdown in regions away from the pit. The results provide direct evidence of the ability of localized defects to decrease the barrier to dielectric breakdown in an ordered oxide film.

9:20am **SS1+MC-ThM4 Oxidation of Sn/Pt (111) Surface Alloys under UHV Conditions- Formation of Ultrathin SnOx Films on Pt(111)***, M. Batzill, D. Beck, **B.E. Koel**,* University of Southern California

Platinum-tin systems are important as hydrocarbon reforming catalysts when supported on alumina. The tin may however exist in oxidic form and thus SnOx may be responsible for the altered catalytic properties of the Sn-Pt system compared to pure Pt, rather than alloying of Sn and Pt. In order to study ultrathin SnOx overlayers on Platinum we have oxidized both ordered Sn/Pt(111) surface alloys (the p(2x2) and the (sqr3 x sqr3)R30 alloy structure) using NO2 as an oxidant. The structure, chemical state and thermal stability of the oxide films have been examined by LEED, STM, XPS, AES and TPD. Oxidation of p(2x2) alloy results in a discontinuous mono-layer thick SnOx film that decomposes at 760 K. Oxidation of the (sqr3 x sqr3)R30 in contrast forms a thermally more stable continuous overlayer that shows two ordered surface phases depending on the annealing temperature. These structures have been analyzed using LEED and STM. The chemical activity of these surfaces was probed by small hydrocarbon molecules and CO.

9:40am **SS1+MC-ThM5 Monte Carlo Simulation of Initial Al(111) Oxidation***, **D.E. Oner**, R. Chakarova, I. Zori@aa c@, B. Kasemo,* Chalmers University of Technology, Sweden

In this work a Monte Carlo simulation technique is applied, exploring the influence of several models for O@sub 2@ dissociation on the initial Al(111) oxidation. The primary experimental data motivating this are the STM studies by Brune et al. (J. Chem. Phys. 99 (1993) 2128). The simulations are performed to gain more insight into the kinetics of the oxidation process. The Monte Carlo simulation is based on the lattice-gas approach using the Metropolis algorithm. The simulations assume alternatively "normal" dissociation (deposition of O atoms at adjacent surface sites), hot dimer dissociation (widely separated O atoms due to hot dissociation fragments) or abstraction (one of the separating O atoms performs a ballistic motion away from the surface). Further elements of the model are surface mobility, attractive forces between adsorbed O-atoms (i.e. adsorbate-adsorbate interaction), and in-diffusion of O atoms into the 2nd and deeper layers to form 2D and 3D oxide. Input data are, when available, taken from experiments or first-principles calculations. The results of this computational work are compared to the experimental results by Brune et al. The calculated surface configurations of chemisorbed O-atoms at 300 K in the low coverage regime, based on the hot dimer dissociation model, are in good agreement with the observed experimental STM data. The simulations of thermal annealing of chemisorbed oxygen islands are in fair agreement with the observed island kinetics by Trost et al. (J. Chem. Phys. 108 (1998) 1740). In the latter case, the O-O interaction strength is a crucial parameter. The present simulation model provides a useful platform for further simulations of Al oxidation. @FootnoteText@ Keywords: Monte Carlo simulation, surface oxidation, oxide nucleation and growth, hot chemisorption, metal oxidation, kinetics, aluminium.

10:00am **SS1+MC-ThM6 Thin Epitaxial Oxide Films and Interfaces for Advanced Microlectronics and Magnetics**, ***S.A. Chambers,*** Pacific Northwest National Laboratory **INVITED**

Metal oxides constitute an extremely diverse class of materials, with virtually all types of electronic and magnetic behavior represented. These materials thus possess many properties that make them unique and potentially important for future technologies. No other class of materials exhibits such a wide range of behavior: band gaps spanning the visible and UV; electronic properties ranging from superconducting to metallic to semiconducting to insulating; magnetic properties ranging from ferromagnetic to antiferroma gnetic; and dielectric properties ranging from low-k to ferroelectric and piezoelectric. In addition, metal oxides exhibit a wide range of crystal structures, including spinel, perovskite, and corundum. As a result, a variety of heteroepitaxial structures can be designed and synthesized. In this talk, I present recent results on three heteroepitaxial oxide systems that illustrate the fascinating interface physics and potential technological advantages of these materials: (1) SrTiO@sub 3@(001)/Si(001), (2) CoFe@sub 2@O@sub 4@(001)/MgO(001) and, (3) MgO(001)/Ag(001) and Pt(111)/@alpha@-Cr@sub 2@O@sub 3@(0001)/Pt(111)/@alpha@-Al@sub 2@O@sub 3@(0001). System 1 is of considerable interest as a high-k gate oxide in next-generation MOSFETs.@footnote 1@ System 2 is a model that permits us to investigate thin films of what appears to be a very promising high-magnetic-anisotropy, insulating ferrimagnet.@footnote 2@ System 3 allows us to examine the effects of polarizable metals on the optical, electronic and magnetic properties of ultrathin oxides that are within electronic screening lengths of the metal.@footnote 3@ Structural, electronic and magnetic properties of these systems, all grown by molecular beam epitaxy, will be presented. @FootnoteText@ @footnote 1@ R.A. KcKee et al., Phys. Rev. Lett. 72, 2741 (1994). @footnote 2@ Y. Suzuki et al., Appl. Phys. Lett. 68, 714 (1996). @footnote 3@ S. Altieri et al., Phys. Rev. B59, R2517 (1999).

10:40am **SS1+MC-ThM8 The Oxidation of Pd(100)**, ***G. Zheng***, *E.I. Altman,* Yale University

Motivated by interest in Pd as a catalyst for oxidation reactions and the catalytic combustion of CH@sub 4@, the interaction of Pd(100) with O@sub 2@ was studied using LEED, STM, and TPD. Initial exposure of Pd(100) to O@sub 2@ at room temperature resulted in a (2x2) structure that saturated at an oxygen coverage of 0.25 ML (1 ML = 1 O/Surface Pd) following 30 L exposure. Further exposure to O@sub 2@ at room temperature resulted in a mixture of (2x2) and p(5x5) LEED patterns, which persisted until the oxygen coverage reached a saturation value of 0.68 ML. Increasing the exposure temperature to 475 K resulted in the p(5x5) structure in the oxygen coverage range of 0.60-0.80 ML, which transformed into a (@sr@5x@sr@5)R27° pattern beyond 0.80 ML. TPD experiments revealed four oxygen desorption features from Pd(100) following exposure to O@sub 2@, including peaks at 800 K, 700 K and 650 K, as well as a low temperature oxygen shoulder at 600 K. The highest temperature peak corresponds to the (2x2) chemisorption structure, and the other two peaks fall into the regime where p(5x5) and (@sr@5x@sr@5)R27° patterns appear. The three peaks saturated in sequence, and the low temperature shoulder showed up before saturation of the 650 K peak. These results indicate at least four distinct oxygen states on Pd(100). Upon annealing, the (@sr@5x@sr@5)R27° LEED pattern transformed into the (2x2) pattern without stepping through the p(5x5), and the p(5x5) structure converted into the (2x2) pattern. The temperature dependence of oxygen up-take was also studied. Oxygen was found to have the highest sticking coefficient on Pd(100) at 550 K. STM studies revealed the atomic structures of various oxygen phases on Pd(100), as well as their relative reactivity towards reduction by in-situ monitoring of the surface during exposure to CO and propylene.

11:00am **SS1+MC-ThM9 Surface Characterization of Oxidative Corrosion of U-Nb Alloys**, ***D. Kelly,*** Los Alamos National Laboratory*; W.L. Manner,* Union Carbide Corporation*; J.A. Lillard, R.J. Hanrahan, Jr., M.T. Paffett,* Los Alamos National Laboratory

We have studied the relative rates of oxidative corrosion of U-Nb alloys containing 2 to 8 wt. % Nb, using X-ray photoelectron spectroscopy (XPS) and depth profiling by sputtered neutrals mass spectroscopy (SNMS), The alloys have been characterized after exposure to dry and humidified air (up to 50% relative humidity) at temperatures from 25 to 125 @super o@C, and exposure to electrochemical solutions. XPS studies of U-6 wt. % Nb following oxidation at 300 K with oxygen indicate formation of a thin overlayer of stoichiometric UO@sub 2@ intermixed with Nb@sub 2@O@sub 5@. This same stoichiometry is exhibited upon oxygen treatment at 500 K, however, niobium is much less oxidized, forming a mixture of NbO and Nb. SNMS depth profiling indicates that oxides formed using oxygen are thicker than those obtained using water. The formation of a critical density of Nb@sub 2@O@sub 5@ is suggested to enhance corrosion resistance by preventing diffusion of oxygen and/or hydroxyl species into the oxide/metal interface region. Tube furnace oxidation of the U-Nb alloys produces oxide layers comprised of UO@sub 2@ and Nb@sub 2@O@sub 5@ under all experimental conditions used. The thickness of the oxides increased with treatment time and temperature, but decreased with increasing Nb alloy content. For example, a 48 hour treatment at 75 @super o@C and 50% relative humidity results in oxide thickness on U-2%Nb that are three times that on U-8%Nb. Electrochemical oxidation of U-Nb alloys facilely generated UO@sub 3@ and Nb@sub 2@O@sub 5@ oxide layers with thicknesses qualitatively similar to thermal oxidation results. U-Nb alloys electrochemically oxidized at low pH exhibit oxide layers with near-surface regions (50 ???) enhanced in Nb content, as compared to the bulk material. Surface UO@sub 3@ was not readily reduced upon exposure to molecular D@sub 2@; however, D atoms facilely reduced UO@sub 3@ to UO@sub 2@.

11:20am **SS1+MC-ThM10 AFM Non-contact Imaging of Titaniumdioxid at Variable Temperatures**, *A. Bettac,* ***P. Güthner****, S. Molitor, A. Feltz, T. Berghaus,* Omicron Vakuumphysik GmbH, Germany*; A.W. Grant, S. Fain,* University of Washington

True atomic resolution in AFM non-contact mode has been achieved on several samples. Here we present first images on a TiO@sub 2@ (110) single crystal at sample temperatures from as low as 50 K up to 400° C. A new instrument design allows to perform true atomic resolution AFM images in a temperature range from 25 K to 1000 K. The sample was prepared by several cycles of ion sputtering and annealing in UHV. After this treatment it is conducting enough to perform STM measurements for controlling the quality of surface preparation. Non-contact AFM images on the TiO@sub 2@ (110) crystal show atomic resolution across mono-atomic steps. The surface is mostly showing a 1x1 reconstruction. At the step edges, lines with 1x2 reconstruction are starting. These lines may be associated with the formation of Ti@sub 2@O@sub 3@ strings along the surface. The density of areas with 1x2 reconstruction is increased with the annealing temperature which can be explained by the desorbtion of oxygen during the annealing process. Atomic resolution images on the TiO@sub 2@ (110) crystal were achieved at low temperatures down to 50 K sample temperature and at high temperatures up to 400° C.

11:40am **SS1+MC-ThM11 Plasma Oxidation as a Tool to Design Oxide Films at Low Temperatures**, ***R. Schennach,*** Lamar University*; D.G. Naugle,* Texas A&M University*; H. McWhinney,* Prairie View A&M University*; D.L. Cocke,* Lamar University

Interfacial oxidation is an established approach to produce surface thin films for catalysts, corrosion, ware protective coatings and electronic structures. The three main oxidation methods: thermal, anodic and plasma, still lack adequate fundamental physical-chemical models that can allow film design, particularly on alloys. Plasma oxidation of a CuZr alloy is studied using XPS (X-ray Photoelectron Spectroscopy). The dependence of the resulting oxide film on alloy composition and sample temperature during plasma oxidation is investigated. In contrast to thermal and electrochemical oxidation which lead to the formation of a zirconium oxide film, plasma oxidation leads to the formation of a copper oxide or metallic copper over layer depending on temperature and copper concentration in the bulk. It is shown that plasma oxidation can be used to design oxide films at room temperature, which require high temperatures using thermal oxidation.

Surface Science
Room 209 - Session SS2+VT-ThM

Adsorption and Desorption Phenomena II

Moderator: J.C. Hemminger, University of California, Irvine

8:20am **SS2+VT-ThM1 Alkali Metal and H@sub 2@O Co-adsorption and Reaction on Graphite(0001)**, ***M.A. Gleeson****, D.V. Chakarov, B. Kasemo,* Chalmers University of Technology and Göteborg University, Sweden

A comparative study of alkali metal (Na, K, Cs) adsorption, co-adsorption and reaction with H@sub 2@O on the basal plane of graphite has been performed. Water molecules are stabilised by interaction with alkali atoms, and undergo coverage and temperature dependent reactions. The surface solvation number is similar for all three alkali metals at low coverages (3 to 4 H@sub 2@O molecules per alkali atom). The critical alkali coverage for reactive co-adsorption at 98 K ranges between 0.1 to 0.25 ML. Reaction between H@sub 2@O and the alkali metals leads to the formation of hydroxide, hydride and oxide species on the surface. Additional peaks appear in the water desorption spectra due to alkali-stabilised H@sub 2@O and hydroxide decomposition. Decomposition of alkali oxides at high temperature can result in oxidation of the graphite and subsequent CO@sub 2@ evolution. Similarities and differences between the alkali metals are discussed.

8:40am **SS2+VT-ThM2 Adsorption of Hydrogen on Clean and Alkali-modified Low-index and Stepped Copper Surfaces***, L. Thomsen,* Odense University/University of Southern Denmark*; **J. Onsgaard,*** Odense University/University of Southern Denmark, Denmark*; P.J. Godowski,* University of Wroclaw, Poland*; S.V. Hoffmann,* University of Aarhus, Denmark*; L. Bech, P. Moller,* Odense University/University of Southern Denmark

The interest for adsorption of low molecular gases like H and CO@sub 2@ on alkali-modified copper surfaces stems from the promoting role of the alkali metals in heterogeneous catalysis. Due to the substantial lowering of the work function with the addition of the alkali metal, pronounced changes in the adsorption and reaction properties of the copper surfaces are observed. The adsorption of atomic hydrogen on clean and potassium-modified Cu(110), Cu(100) surfaces and the stepped Cu(115), Cu(117) and Cu(112) surfaces has been studied. Typically, two hydrogen-induced states in the valence band have been found on the clean crystal and assigned to one state receding in the subsurface and another state at the surface of the crystal. Two states due to hydrogen are also observed on the potassium-modified surfaces and assigned to a potassium-hydrogen bond and a copper-hydrogen bond. Coadsorption of H and CO@sub 2@ on the K/Cu surface results in formation of formate with high efficiency on the most corrugated surfaces.

9:00am **SS2+VT-ThM3 Angle Resolved Photoemission Study on Adsorption and Desorption of Cobaltocene on Cu(111)***, **J. Choi,*** Louisiana State University*; P.A. Dowben,* University of Nebraska, Lincoln

The molecular adsorption and desorption of cobaltocene, Co(C5H5)2, on Cu(111) have been studied by angle resolved photoemission spectroscopy (ARPES). We have measured the molecular orientation and bonding of adsorbed cobaltocene on Cu(111). Photoemission results indicate that the initially adsorbed surface species closely resembles that of molecular cobaltocene. The shift in photoemission binding energies relative to gas phase is largely independent of the molecular orbital. The molecule is adsorbed with cyclopentadienyl (C5H5) ring ligands parallel to the surface at 150K, and the molecular axis normal to the surface at the low coverage (below 10 Langmuir). The molecularly adsorbed cobaltocene loses the normal preferential orientation, at the higher coverages. Furthermore, molecular orientation is strongly affected by annealing temperature, indicating that there are more than one molecular adsorption states. With increasing of temperature, molecularly adsorbed cobaltocene on Cu(111) is desorbed.

9:20am **SS2+VT-ThM4 Angle Effects on the Nucleation of Polymeric Thin Films from Molecular Cluster Deposition: Molecular Dynamics Simulations***, **Y. Hu,** S.B. Sinnott,* The University of Kentucky

Cluster beam deposition of organic material is thought to result in thin-film formation through rapid chemical reactions that occur at the impact site between the cluster and the surface. These reactions occur on the order of a few picoseconds and so are ideal for study with atomistic simulations. In this work, classical molecular dynamics simulations are used to investigate the effect of incident angle on the nucleation and growth of polymeric thin films through organic molecular cluster deposition. The classical reactive empirical bond order method is used in the simulations.@footnote 1@ The specific system under study consists of clusters of ethylene being deposited on a diamond and amorphous carbon substrate at room temperature at various incident angles. The results show how the incident angle affects the nucleation of a thin film from the deposition. In addition, the dependence of this angle effect on substrate rigidity is investigated. This work is supported by the National Science Foundation (CHE-9708049). @FootnoteText@ @footnote 1@ S.B. Sinnott, L. Qi, O.A. Shenderova, D.W. Brenner, in Chapter 1 of Volume IV of ADVANCES IN CLASSICAL TRAJECTORY METHODS, Molecular Dynamics of Clusters, Surfaces, Liquids, and Interfaces, Ed. W. Hase (JAI Press, Inc., Stamford, CT, 1999), pp. 1-26.

9:40am **SS2+VT-ThM5 Geometrical Structure and Orientation of Metal Tetraphenylporphyrins on Au (111)***, K.W. Hipps, **L. Scudiero,** D.E. Barlow,* Washington State University

Geometrical structure and orientation of metal tetraphenylporphyrins on Au (111). Metal (II) tetraphenylporphyrin (MTPP) complexes adsorbed on polycrystalline Au and Au (111) are studied by Fourier transform reflectance-absorption infrared (FT-RAIR), X-ray Photoelectron Spectroscopy (XPS) and Scanning Tunneling Microscope (STM). XPS and FT-RAIR data indicate that the chemical composition of those complexes is preserved when they are vapor deposited on Au. FT-RAIR data also suggests that the first few adsorbed layers are oriented with the porphyrin ring parallel to the Au surface. STM images are presented for several transition metal ions. At low coverage, STM images show monolayer islands randomly distributed on Au (111) and high-resolution images display a square unit cell.

10:00am **SS2+VT-ThM6 Experimental and Theoretical STM Imaging of Xylene Isomers on Pd(111)@footnote 1@***, D. Futaba, J.P. Landry, **A. Loui,** S. Chiang,* University of California, Davis

We have performed both theoretical and experimental studies of the three isomers of xylene, C@sub 6@H @sub 4@(CH@sub 3@)@sub 2@, adsorbed on Pd(111). Simulated scanning tunneling microscope (STM) images, calculated using a relatively simple computational method based on extended Hückel molecular orbital theory (EHT), showed no observable differences in surface features between occupied and unoccupied states images, nor between adsorption on the various high symmetry binding sites. The calculated binding energies suggest that xylene molecules prefer to bind in particular orientations on hollow and bridge sites. The computed images for xylene on Pd displayed almost identical surface features and symmetries as those calculated on Rh(111).@footnote 2@ Using STM and low-energy electron diffraction (LEED), we imaged the characteristic surface structures and investigated the molecular ordering for the three isomers on Pd(111). Experimental STM images showed each of the isomers exhibiting the characteristic geometries predicted by EHT. Both meta(m-)xylene and ortho(o-)xylene are characterized by an overall triangular shape, with m-xylene nearly equilateral. Para(p-)xylene shows a distinct diamond shape. M-xylene molecules adsorbed to upper step edges, usually with one side of the molecule aligned with the step edge and parallel to the close-packed directions of the Pd lattice. Only the p-xylene isomer showed long range order, forming a hexagonal structure with the long axes of the molecules parallel to each other. Translation and rotation of p-xylene molecules between consecutive scans were observed for the saturated Pd surface, causing disorder in previously ordered regions. @FootnoteText@ @footnote 1@ Supported by NSF CHE-95-20366 and UCOP CLC. @footnote 2@ D. N. Futaba and S. Chiang, Surf. Sci., 448, L175 (2000).

10:20am **SS2+VT-ThM7 Reactions of cis-, trans-, and 1,1-dichloroethene on Pd(111) Studied by TDS, LITD, and STM***, D.E. Hunka, D.M. Jaramillo,* University of California, Davis*; D.C. Herman,* University of North Carolina, Chapel Hill*; K.D. Lormand, D. Futaba, S. Chiang, **D.P. Land,*** University of California, Davis

Chloroethylenes are the among the most abundant groundwater and soil contaminants. Catalytic degradation on transition metal surfaces offers a promising method for the alleviation of this ubiquitous problem. Large differences in the reaction rates of the various compounds have been observed. However, little is known about the reaction mechanisms or the origin of these rate differences. In aqueous solutions, for example, cis-dichloroethylene (cis-DCE) reacts an order of magnitude more slowly on Fe than do trans- or 1,1-DCE. The reactivities do not follow any monotonic trends in dipole, solubility, or bond strength. Addition of Pd to Fe catalysts has been shown to increase the rate of reaction for some of these species by orders of magnitude. We have undertaken to study the reactivity of the three isomers of DCE on Pd(111). As in aqueous solution, the cis isomer reacts very differently from the other two isomers. Decomposition on Pd(111) occurs below room temperature and H@sub 2@ is evolved with C and Cl remaining on the surface to very high temperatures. In contrast, both trans- and 1,1-DCE rearrange to yield chlorinated intermediates that decompose in two steps above room temperature liberating HCl. Some subtle differences exist in the reaction mechanisms, but both are drastically different from the cis isomer. Laser-induced thermal desorption and conventional thermal desorption with FT mass spectrometry, infrared spectroscopy, scannin tunneling microscopy and other surface techniques are used to elucidate the surface reaction mechanisms and energetics.

10:40am **SS2+VT-ThM8 Wet Oxidation of CO on Pt(111)***, **J. Bergeld**, D.V. Chakarov, B. Kasemo,* Chalmers University of Technology and Göteborg University, Sweden

Presence of small amounts of OH is found to initiate the CO oxidation on Pt(111) surface. We have studied water coadsorption with CO on atomic oxygen precovered platinum surface with temperature programmed desorption (TPD) and found distinct relationship between the low temperature, @beta@@sub 3@ peak intensity and the presence and amount of coadsorbed OH. High initial CO coverage is another prerequisite for the low temperature start of the reaction. We are proposing and discussing several feasible mechanisms of the phenomenon, giving preference to autocatalytic reaction between CO and OH at the boundaries of ordered CO and oxygen/hydroxyl islands.

11:00am **SS2+VT-ThM9 The Behavior of Zirconium Surfaces in the Presence of Oxygen, Nitrogen, and Hydrogen Containing Adsorbates***, **Y.C. Kang**, D.A. Clauss, R.D. Ramsier,* University of Akron

Zirconium and its alloys exhibit a unique combination of physical properties that have led to their widespread use as structural materials in fission reactors as well as in a variety of chemical engineering applications involving harsh environments. Common to these applications is the presence of oxygen, nitrogen, and hydrogen containing moieties. Mechanistic studies of the chemistry of such species on zirconium surfaces are necessary to answer fundamental questions which cannot be addressed by phenomenological models of environmentally assisted degradation in these systems. As part of an effort to address these questions, low energy electron diffraction (LEED) and temperature programmed desorption (TPD) techniques have been applied to the adsorption of water, nitric oxide, and ammonia on Zr(0001) surfaces. Water adsorption at 180 K at exposures above 0.75 L results in water desorption in a broad TPD feature near 550 K. Data from LEED indicate that this adsorption does not result in ordered layers until 700 K annealing, and that the formation of ordered structures depends on exposure and annealing conditions. Low exposures of nitric oxide and ammonia at 160 K results in essentially no thermal desorption features, but high (greater than 20 L) ammonia exposures results in the production of water during TPD experiments and the formation of complex residual LEED patterns. These TPD and LEED data indicate a competition between the kinetics of recombination and desorption with those of diffusion involving the near-surface regions.

11:20am **SS2+VT-ThM10 Chlorosilane Adsorption on Clean Si Surfaces: STM and FT-IR Studies***, **M. Nishizawa**, T. Yasuda, S. Yamasaki,* Joint Research Center for Atom Technology (JRCAT), Japan*; M. Shinohara, Y. Kimura, M. Niwano,* Research Institute of Electrical Communication (RIEC), Japan

Understanding the interaction of silane and chlorosilane molecules, (SiH@sub n@Cl@sub 4-n@), with Si surfaces is the base for atomic-scale control of Si growth. A Si(111) surface exhibits the DAS structure which has 7 kinds of dangling bonds with different electron occupancy, while a Si(100) surface reconstructs to the asymmetric-dimer structure. We are interested in the interaction of chlorosilane with these qualitatively different surfaces. This paper discusses structures of SiH@sub 2@Cl@sub 2@-chemisorbed Si(111)-(7x7) and Si(100)-(2x1) surfaces. We have employed STM to identify reaction sites, and FT-IR to probe their local structure. In the STM topographs for adsorption on the Si(111)-(7x7) surface, reacted adatom sites appear darker than the unreacted ones. At a low coverage, we find that SiH@sub 2@Cl@sub 2@ molecules preferentially react with corner adatoms in the unfaulted half of the (7x7) unit cell to produce surface species - SiH@sub 2@Cl and -Cl. Komura et al. proposed a structural model in which the - SiH@sub 2@Cl group is adsorbed on the corner-hole atom.@footnote 1@ Our STM results agree with this model. On the other hand, FT-IR spectra measured for this surface showed two sharp peaks at 2108 cm@super -1@ and 2123 cm@super -1@. These peaks are tentatively assigned to the symmetric and asymmetric Si-H stretching vibrations of the surface - SiH@sub 2@Cl group. However, the observed peak positions of the Si-H stretching vibrations are much lower than those predicted from the semi-empirical formula by Locovsky.@footnote 2@ The reason for this discrepancy is under consideration. Results for the Si(100) surface will be reported at the presentation. This study, partly supported by NEDO, was performed at JRCAT under the joint research agreement between NAIR and ATP. @FootnoteText@ @footnote 1@ T. Komura et al., Appl Surf. Sci. 130 (1998) 23. @footnote 2@ G. Lucovsky, Solid State Commun. 29 (1979) 571.

11:40am **SS2+VT-ThM11 A Far-IRAS Study of Water Adsorption on V@sub2@O@sub3@(0001)***, **M.J. Pilling**,* University of Wisconsin, Milwaukee*; D.S. Toledano,* Yale University*; C.J. Hirschmugl,* University of Wisconsin, Milwaukee*; V.E. Henrich,* Yale University

The high brightness of a synchrotron radiation source has been utilized to investigate adsorption occurring on a single crystal transition metal oxide surface with far infrared reflection absorption spectroscopy (IRAS). The adsorption of H@sub2@O, H@sub2@@super18@O and oxygen on V@sub2@O@sub3@(0001) was investigated between 154K and 224K. Infrared absorption bands at 992 cm@super-1@ and 1040cm@super-1@ are observed in the spectra above and below the desorption temperature of multilayer water, indicating the presence of a chemisorbed surface species.

Surface Science
Room 210 - Session SS3-ThM
Surface and Interface Structure II

Moderator: A.P. Baddorf, Oak Ridge National Laboratory

8:20am **SS3-ThM1 Polar Oxide Surfaces***, **M. Gajdardziska-Josifovska**,* University of Wisconsin, Milwaukee **INVITED**

The stability of polar oxide surfaces has long been a problematic question in surface science. A bulk terminated polar surface has an infinite surface energy because alternating layers of oppositely charged ions produce a large dipole moment perpendicular to the surface. Such a singularity presents many interesting questions ranging from the fundamental "Can polar oxide surfaces exist?" via the mechanistic "How can they get stabilized?" to the applied "Would they have unique and useful surface and interface properties?". Both theory and experiment have provided several contrary answers to the first two questions, and the last is largely unexplored. In the seventies, the problem was considered closed with consensus between theory and experiment that polar oxide surfaces can not exist but must facet into neutral planes to gain finite surface energy. In the nineties the problem was reopened with experimental discoveries of reconstructed polar oxide surfaces and with theoretical predictions of clean reconstructed surfaces based on the idea of smallest neutral building blocks. At present, there is disagreement between the few proposed and solved polar oxide surface structures, and the reconstruction mechanism is under construction. An additional controversy surrounds the 1x1 structure of polar oxide surfaces. Classical electrostatic approaches predict that such structures can exist only by adsorption of charged species, OH being the currently favored termination, but quantum mechanical approaches predict two dimensional surface metalization of the clean 1x1 surface. I will review the present state of knowledge, with illustrations from our multi-technique experimental studies of the polar MgO and NiO (111) surfaces and their neutral (100) and (110) counterparts. Our data favors the reconstruction mechanism at high temperatures, and the OH adsorption mechanism at lower temperatures.

9:00am **SS3-ThM3 Helium Atom Scattering Study of the Surface Structure and Dynamics of in situ Cleaved MgO(001) Single Crystals@footnote 1@***, **J.G. Skofronick**,* Florida State University*; G. Benedek,* Dipartimento di Fisica dell'Universita'*; G. Brusdeylins, D. Schmicker, S. Schmidt, V. Senz, J.P. Toennies, F. Traeger, R. Vollmer,* Max-Planck-Institute fuer Stroemungsforschung, Germany

A high resolution helium atom scattering study on the surface structure and dynamics of in situ cleaved MgO(001) single crystals, under ultra high vacuum conditions, in both high symmetry directions, has been performed. The Rayleigh modes were observed over most of the reduced surface Brillouin zone; these results agree with previous measurements and theory. Two new modes at and near the zone boundary for the and the high symmetry directions are observed at 40 meV and 36 meV, respectively. A weak half order reconstruction is observed in diffraction scans in the direction. A suggested mechanism for the latter is given. Refined bound state resonance information, giving the energy levels of the laterally averaged He+MgO(001) surface potential are included. @FootnoteText@ @footnote 1@ Supported in part (JGS) by DOE Grant No. DE-FG02-97ER45635.

9:20am **SS3-ThM4 Molecular Beam Epitaxy-Scanning Tunneling Microscopy of Wurtzite GaN Thin Films***, **Q.Z. Xue**, Q.K. Xue, S. Kuwano, K.F. Kelly, S. Nakayama, I.S.T. Tsong, T. Sakurai,* Tohoku University, Japan*; T. Ohno,* National Research Institute of Metals, Japan

Gallium nitride has been known for their enormous potential applications for optoelectronics devices operating in the spectral range from blue to ultraviolet. As the present application depends critically on controlled heteroepitaxy of GaN thin films, complete knowledge of its growth behavior and fundamental physical properties is highly desired to optimize its film growth and device applications. GaN can crystallize into both hexagonal and cubic forms, depending on the substrates and the growth conditions. And the hexagonal GaN has a further freedom in its film polarity, which has direct influence on its surface structure and growth process. In the present work, a systematic investigation of the growth and the surface reconstructions of the wurtzite GaN have been in-situ performed using molecular beam epitaxy (MBE) combined with scanning tunneling microscopy (STM) system. A two-step method is developed to prepare the 6H-SiC substrate, and the Ga-polar GaN(0001) and N-polar thin films are grown by plasma-assisted-MBE on the Si-polar and C-polar 6H-SiC respectively. Through the post-growth Ga-deposition, distinctly different series of surface reconstructions have been obtained on the films for each polarity, that is, on GaN(0001) surface, 1x1, 2x2, 4x4, @sr@7x@sr@7, 5x5, 5@sr@3x2@sr@13, 10x10 and 1x1-Ga fluid are formed, while on GaN(000-1) surface, 2x4, 6x6, 2@sr@7x2@sr@7 are observed. All these phases are Ga-rich, and no ordered N-rich phase has been observed. Based on the atomically-resolved STM images and first principles total energy calculations, we will show that the structures of these phases can be understood under Ga-adatom scheme. Since many of them are not satisfied with electron counting which is popular for the conventional semiconductors, we will document that stability of these phases can be interpreted by Peierls or Mott-Hubbard metal-insulator transitions due to the many-body effects.

9:40am **SS3-ThM5 One-Dimensional Noble Metal Growth on Si(5 5 12)***, **A.A. Baski**, K.M. Jones, K.M. Saoud,* Virginia Commonwealth University **INVITED**

Metal-semiconductor systems that exhibit 1-D growth have lately been of interest, particularly those that form nanometer-scale metal rows on a semiconductor. The recently discovered surface of Si(5 5 12) forms a single-domain reconstruction composed of row-like structures.@footnote 1@ providing a unique template for the growth of 1-D nanostructures. Our recent scanning tunneling microscopy (STM) studies show that noble metals such as Ag and Au deposited onto Si(5 5 12) and annealed indeed form a wide variety of well-ordered overlayer rows.@footnote 2@ At coverages below 0.25 monolayers (ML), both metals grow as monatomic rows with an inter-row spacing of ~5 nm. These metal rows preferentially nucleate along the more reactive Si tetramer rows of the surface reconstruction, leading to their growth in a periodic array. Scanning tunneling spectroscopy (STS) data show that Ag wires have a finite density of states at zero volts, indicating metallic behavior. At higher coverages and annealing temperatures, the underlying Si reconstruction is removed and the growth behavior of Ag and Au diverges. Up to ~0.5 ML, Ag forms sawtooth rows which evolve with coverage to an extremely well-ordered array of stepped double rows. Surprisingly, this phase has a significant band gap (1.25 V) compared to the clean Si surface (0.5 V). At comparable coverages and annealing temperatures, Au growth is usually less ordered; however, significantly elevated temperatures (>500C) lead to the creation of well-ordered facet planes [e.g. (7 7 15) and (225)]. For all coverages and annealing temperatures studied here, deposits of Au and Ag form row-like morphologies on the Si(5 5 12) surface, indicating the utility of this high-index surface as a template for the growth of 1-D nanostructures. @FootnoteText@ @footnote 1@ A. A. Baski, S. C. Erwin, and L. J. Whitman, Science 269, 1556 (1995). @footnote 2@ H.H. Song, K.M. Jones, and A.A. Baski, J. Vac. Sci. Technol. A 17(4), 1696 (1999).

10:20am **SS3-ThM7 Stability and Nuclear Formation of Si(111)-7x7 Structure as Determined from Charge Redistribution in Surface Layers***, **K. Miyake**, T. Kaikoh, Y.J. Li,* University of Tsukuba, Japan*; R. Morita, M. Yamashita,* Hokkaido University, Japan*; H. Shigekawa,* University of Tsukuba, Japan

Reconstruction of the Si(111) surface has been extensively studied by various experiments as well as theoretical considerations. And 7x7 structure has been concluded to be the most stable phase on the Si(111) surface in equilibrium condition. In fact, the 7x7 phase is completed on the well annealed surface, and phase transition between high-temperature "1x1" and 7x7 phases was directly observed around the critical temperature by using scanning tunneling microscopy (STM). The dimer-adatomstacking-fault (DAS) structure proposed by Takayanagi et al., @footnote 1@ which is compatible with the experimental and theoretical results, is widely accepted as the model for the Si(111)-7x7 reconstructed surface structure. And atomic arrangement of the DAS structure in the static form is now well established. However, since the DAS structure involves few surface layers and is very complicated, dynamics of the surface, mechanism for the formation and stabilizing processes of the structure, has not yet been completely clarified, and is still attracting considerable attention. By considering the charge transfer from adatoms to rest atoms, we can analyze the structure of the dimer and stacking-fault (DS) layers in the Si(111) dimer-adatomstacking-fault (DAS) structure in a subunit level. In comparison with the modified model of Vanderbilt, corner holes with the completed DS structure in the second layer, completed corner hole, was confirmed to play a key role not only in the mechanism to stabilize the DAS structure, but also in the formation process of it; formation of the completed corner hole works as a rate limiting process for the growth of the DAS structure.@footnote 2@ This mechanism was shown to be quite consistent with the experimental results which had been obtained by STM on the quenched and HBO@SUB 2@ molecules irradiated Si(111) surface.@footnote 3@ Phase transition from Si(111)-7x7 to the B-induced @sr@3x@sr@3 structure, and the structure near the step edge was analyzed in detail. @FootnoteText@ @footnote 1@K. Takayanagi et al, J. Vac. Sci. Technol., A 3 (1985) 1502. @footnote 2@K. Miyake et al., Surf. Sci., 429 (1999) 260-273. @footnote 3@K. Miyake et al., Jpn. J. Appl. Phys., 38 (1999) 3841.

10:40am **SS3-ThM8 First Principles Study of Cross-sectional Surface Structure of III-V Heterostructures***, **S.-G. Kim**,* Vanderbilt University*; S.C. Erwin, B.Z. Nosho, L.J. Whitman,* Naval Research Laboratory

Heterostructures of III-V semiconductors form the basis for a variety of devices. The performance of these multilayer structures is extremely sensitive to the thickness of the layers and the nature of the interfaces between them. As the layers are made thinner, a microscopic understanding of interface structure and chemistry will become increasingly important for optimizing device performance. The challenge is how best to achieve a complete microscopic characterization. We demonstrate the power of combining density-functional theory with experimental data from cross-sectional scanning tunneling microscopy (XSTM). We use first-principles computational methods to interpret XSTM images that we have obtained from the (110) cleavage surface of 6.1-Å III-V heterostructures. We begin by determining theoretically the fully relaxed geometry of cleaved InAs/GaSb superlattices, using the local-density approximation (LDA) to density-functional theory. To understand the relative importance of electronic vs. structural effects in the STM topography, we generate simulated XSTM images over the cross-sectional surface and compare with our measured XSTM images. We also focus on the role played by the specific interface bond type (In-Sb vs. Ga-As bonds) and show, for example, that XSTM can indeed be used reliably to identify the interface bond type. Finally, we study in detail the thermodynamics of defect formation due to diffusion across the interface; these theoretical predictions compare very favorably with our XSTM studies, and form the basis for further studies of the impact of interfacial disorder on device performance.

11:00am **SS3-ThM9 Reflectance Difference Spectroscopy of Mixed Arsenic-Rich Phases of Gallium Arsenide (001)***, **D.C. Law**, M.J. Begarney,* University of California, Los Angeles*; L. Li,* University of Wisconsin, Milwaukee*; C.H. Li, Q. Fu, R.F. Hicks,* University of California, Los Angeles

The relationship between the reflectance difference spectra and the atomic structure of arsenic-rich reconstructions of GaAs (001) has been investigated. Scanning tunneling micrographs reveal that a complex roughening process occurs as the surface structure changes with decreasing arsenic coverage from 1.75 to 0.75 monolayers (ML). With the loss of 0.1 ML of As, small pits, one bilayer in depth and having the same c(4x4) reconstruction as the top layer, form in the terraces. At the same time, gallium atoms are liberated to the surface, disrupting the c(4x4) ordering. With further arsenic loss, (2x4) domains nucleate and grow on top of the c(4x4). This underlying layer gradually decomposes into a metastable (2xn) phase, and finally into the (2x4). In the reflectance difference spectra, negative peaks at 2.25 and 2.8 eV correlate with the c(4x4)-like arsenic dimers. However, the intensity of the latter feature strongly depends on the presence of adsorbates, such as alkyl groups and gallium adatoms. A positive peak at 3.25 eV appears to be related to the (2xn) structure. Finally, the intensity of the positive peak at 2.9 eV is shown to be proportional to the density of (2x4)-type dimers.

11:20am **SS3-ThM10 Dynamics of the Flip-Flop Motion of Single Buckled Dimers of Si(100)***, **H. Kenji**,* University of Tsukuba, Japan*; M. Ryuji, Y. Mikio,* University of Hokkaido, Japan*; H. Shigekawa,* University of Tsukuba, Japan

We report the direct observation of the flip-flop motion of single buckled dimers of Si(100) in real space by hovering the tunneling tip of scanning tunneling microscope over a pre-selected atom of the flip-flopping dimers and measuring the tunneling current. By this method, the complete time trace of the flip-flop motion of single dimers can be obtained, and from it, any desired properties of the dynamics can be deduced. Each dynamical flip-flop event (up to 200,000) was clearly resolved, and the time trace of the tunneling current shows that the flip-flop motion is a switching between two stable configurations. A statistical analysis of the autocorrelation function elucidates that the flop-flop motion is a stochastic process described by a two level system. The influence of the local environment on the dynamics of the flip-flop motion can be mapped out by executing the measurements on neighboring dimers. We found that the details of the dynamics of the flip-flop motion differ from dimer to dimer and from domain to domain. The activation energy of the flip-flop motion differs significantly (measured 32 meV, estimated 110~ meV) for dimers in different domains. http://dora.ims.tsukuba.ac.jp

11:40am **SS3-ThM11 Molecular Dynamics Simulations of Energetic Silicon Cluster Deposition on Graphite (0001)***, **R. Neuendorf**, R.E. Palmer,* The University of Birmingham, UK*; R. Smith,* Loughborough University, UK

Microcanonical Molecular Dynamics (MD) Simulations using classical interaction potentials@footnote 1@ have been employed to study the deposition of small Silicon clusters (3 to 55 atoms / cluster) onto a graphite (0001) surface. The clusters have been deposited with kinetic energies from 1 eV up to 100 eV per atom. We find that the deposition behaviour can be divided into four different regimes: i) wetting of the substrate for small clusters at low deposition energies leading to the creation of monolayer high isalnds ii) soft landing of larger clusters at low deposition energies iii) implantation of the clusters into the substrate at high deposition energies, leading to "hole drilling" as also found in the case of metal cluster deposition.@footnote 2@ iv) a regime of more complicated behaviour at intermediate deposition energies. @FootnoteText@@footnote 1@S. J. Carroll, S. G. Hall, R. E. Palmer and R. Smith, Phys. Rev. Lett. 81(17), 3715 (1998) @footnote 2@S. J. Carroll, P. D. Nellist, R. E. Palmer, S. Hobday and R. Smith, Phys. Rev. Lett. 84(12), 2654 (2000).

Thin Films
Room 203 - Session TF-ThM
Optical Films

Moderator: W.T. (Pat) Beauchamp, OCLI/JDSU

8:20am **TF-ThM1 Optical Thin Film Multilayer Systems for Thermal Emittance Modulation in the 300K Blackbody Spectral Region***, C.L. Trimble, E.B. Franke,* University of Nebraska, Lincoln*; J.S. Hale,* J.A. Woollam Company, Lincoln*; M. Schubert, **J.A. Woollam**,* University of Nebraska, Lincoln

We report on all-solid state electrochromic multilayer systems for thermal emittance modulation in the 300 K blackbody spectral region (2 to 40 microns). Amorphous and polycrystalline WO@sub 3@ thin films were used as ion storage and electrochromic layers, respectively. Tantalum oxide thin films were used as ion-conductor layers. All films were grown by magnetron sputtering. The multilayer system was switched between low and high emittance states by application of small voltages between two electrodes enclosing the stack, thereby moving previously electrochemically inserted Li@super +@ from the electrochromic to the storage layer and back. Two electrode designs were tested. One was built with an aluminum bottom layer electrode and an aluminum grid top electrode, and a second was made with aluminum grid electrodes on top and bottom. The optical constants of Li@super +@ intercalated and deintercalated tantalum oxide and WO@sub 3@ thin films were measured by ellipsometry from 2 to 35 microns. Prior to experimental layer stack formation, the thin film layer structure was optimized by calculations of emittance modulation based on the single layer optical constants and thicknesses. Performance of the layer stack was obtained by reflectance modulation @DELTA@R from 2 to 40 microns, and related to spectral emittance. Reflectance spectra were further used to calculate the emissivity modulation @DELTA@@epsilon@ integrated over a 300 K blackbody spectrum. Calculations also suggest application of thermal emittance modulating multilayers for temperatures up to 900 K. Additional simulations were performed assuming the layer stack covered by either a ZnS or a MgF@sub 2@ layer. Cover layers should protect the WO@sub 3@ layer, prevent Li@super +@ chemical reactions and moisture incorporation, and act as optical impedance match to improve switching performance. Supported by BMDO # DSAG60-98-C-0054, NASA Glenn Research Center grant # NAG3-2219, and NASA Epscor grant # NCC5-169.

8:40am **TF-ThM2 Structural Characterization of High and Low Index PECVD Optical Coating Materials: The Case of Titanium Dioxide and Silicon Dioxide***, **V. Hajek**, M. Latreche, J.E. Klemberg-Sapieha, L. Martinu,* Ecole Polytechnique, Canada*; A. Argoitia, W.T. Beauchamp,* Optical Coating Laboratory Inc.

In the present work we systematically study the optical, mechanical and structural characteristics of high index TiO@sub2@ and low index SiO@sub2@ films prepared by plasma enhanced chemical vapor deposition (PECVD) under controlled ion bombardment conditions. The films were obtained either individually from titanium tetrachloride (TiCl@sub4@), hexamethyldisiloxane (HMDSO), silicon tetrachloride (SiCl@sub4@) or from TiCl@sub4@/SiCl@sub4@ or TiCl@sub4@/HMDSO mixtures. Depositions were performed using radiofrequency (13.56 MHz) or dual-mode microwave/radiofrequency low pressure plasma systems; the latter one allows for a selective control of the ion energy and ion flux. In the first series of experiments we show that depending on the substrate bias voltage and temperature the refractive index for TiO@sub2@ at 550 nm varies from 2.20 to 2.40, the extinction coefficient remains low (k ~ 1-5 x 10@super-5@), and the film microhardness of about 10 GPa and low stress (0 - 200 MPa in compression) point to good film mechanical integrity. In the second series of experiments we study the transition from amorphous to crystalline structure, chemical bonding, and the role of chlorine in TiO@sub2@, SiO@sub2@ and mixed TiO@sub2@/SiO@sub2@ systems using ERD, XRD, FTIR, microraman, SEM and TEM techniques. The evolution of the microstructure is related to the energetic conditions during the film growth.

9:00am **TF-ThM3 Porous Thin Film Microstructure Control for Tuned Optical Properties***, **J.C. Sit**, S.R. Kennedy, M.J. Brett,* University of Alberta, Canada

The technique of glancing angle deposition (GLAD) has been used to produce highly porous thin film media by exploiting the enhanced atomic self-shadowing encountered with highly oblique angle deposition. Using advanced substrate motion with this technique allows for a great deal of control over the columnar morphology in these porous films. GLAD films with "helical" or chiral morphology have been shown to possess unique optical response including optical rotation and circular dichroism. As the structural parameters of the film determine many of the optical properties, careful control over the structural parameters is critical. For example, the wavelength at which peak optical activity is observed may be engineered to fall within the UV, visible, or NIR regions by appropriate control of the helical pitch. We present here characterization of the optical response with respect to several structural parameters in optical GLAD films including helical pitch and radius. Further, we apply similar characterization to several other microstructural types of interest such as periodically bent nematic (planar "s"-shaped) morphologies.

9:20am **TF-ThM4 Development of a PECVD Antireflective Layer for 193nm Polysilicon Gate Applications***, **W. Fan**, Y. Wang, K. MacWilliams, J. Tian, Z. Karim,* Novellus Systems, Inc., U.S.*; K. Ring,* Conexant Systems, U.S.

A PECVD silicon oxynitride film used as an antireflective layer (ARL) has been developed for patterning sub-0.15µm polysilicon gate at 193nm wavelength. PROLITH/2@super TM@ simulations were carried out to determine the range of optical parameters which results in minimum substrate reflectivity (e.g., a few tenths of one percent). An oxynitride film with n ~ 1.80, k ~ 0.60, and t ~ 260Å, which offers less than 0.1% reflectivity, can be successfully deposited by a typical sequential PECVD chamber. In conjunction with achieving a film with these parameters, film deposition process window, film measurement variation, and post-treatment effects were taken into consideration to ensure minimal reflectivity. Finally, the films were patterned with 193nm photoresists. Cross-section SEM shows tight CD control.

9:40am **TF-ThM5 Characterizing Bi-Layer ARC for Advanced Lithography***, **I. Bloomer**, D.V. Likhachev, J. Lam, D. Harrison,* n&k Technology

Bi-layer ARCs consisting of Si@sub3@N@sub4@/Si-rich SiN@subx@/Si-substrate are gaining attention for advanced lithography applications. Such bi-layer ARCs are more effective than single-layer ARCs in reducing standing waves, and furthermore provide wider processing latitude for overall ARC thickness. The processing conditions for a stoichiometric film such as Si@sub3@N@sub4@ are well controlled, and therefore its index of refraction, n, and the extinction coefficient, k, are well established. By contrast, the n and k values of a silicon-rich SiN@subx@ film are variable and strongly dependent on the gas distribution of the processing chamber. Typically the output is a film with non-uniform composition along the z-axis. For such bi-layer ARCs, rapid and accurate characterization is imperative to produce a consistent, uniform product. We will present a metrology technique, based on the 'n&k Method', that accurately and rapidly characterizes bi-layer ARCs despite variations and non-uniformities. With this method, the thicknesses of both the Si@sub3@N@sub4@ and the non-uniform silicon-rich SiN@subx@ layers are determined simultaneously, along with the n and k spectra (190 to 1000nm) of the non-uniform silicon-rich SiN@subx@ layer, which is determined as a function of z. The â€œn&k Methodâ€ is based on broad-band reflectance that incorporates all-reflective optics to provide a signal-to-noise ratio of better than 0.2% over the entire measured wavelength range of 190 to 1000nm. The Forouhi-Bloomer model for n and k is used to analyze the raw data. Results for a series of samples with silicon-rich SiN@subx@ thicknesses ranging from 180 to 300 Å and the Si@sub3@N@sub4@ thicknesses ranging from 1000 to 1300 Å will be presented, along with the results of the z-direction compositional non-uniformity of the silicon-rich SiN@subx@ layer. We will also discuss how these results can be used to optimize the manufacturing process for bi-layer ARCs.

10:00am **TF-ThM6 A Near-grazing-incidence, Antireflective Coating for 121.6 nm for a Mars-bound Neutral Particle Detector.***, **S. Olson**, D.D. Allred, M.B. Squires, D. Markos, C.E. Mills, R.T. Turley,* Brigham Young University

A neutral particle detector is being planned to orbit Mars as part of the ASPERA mission. It is designed to detect and classify atoms in the exosphere of Mars by their identity and velocity using a time-of-flight mass spectrometer. An electron released on collision with the first surface in the spectrometer (the start surface) initiates a start pulse for the spectrometer. The most significant source of noise is thought to be UV photons-particularly hydrogen Lyman alpha (121.6 nm), which are capable of generating false start and stop pulses. We have design using a genetic algorithm and fabricated a coating for the START surface which absorbs UV photons at 121.6 nm thus preventing their reaching the stop surface. The particular optical challenge was the fact that the particles and incident light arrives at an angle of 10 to 20 degrees from grazing. We will discuss the use of a genetic algorithm in designing the coating, its fabrication, AFM measurements of sample and at-wavelength measurements of their reflectivity.

10:20am **TF-ThM7 Studies of Pulsed DC Power in Magnetron Sputtering Systems***, **P.J. Kelly**, J. O'Brien,* University of Salford, UK*; J.W. Bradley,* UMIST, UK, U.K.*; R. Hall, G. Roche,* Advanced Energy Industries Inc.*; R.D. Arnell,* University of Salford, UK

The application of pulsed DC power has proved to be highly advantageous in magnetron sputtering processes. Indeed, reactive pulsed magnetron sputtering is now amongst the leading techniques for the deposition of dielectric films. When the magnetron discharge is pulsed in the mid-frequency range (20-350kHz), the periodic voltage reversals effectively discharge poisoned regions on the target. This significantly reduces the occurrence of arc events at the target and stabilises the deposition process. As a consequence, substantial improvements have been observed in film structure and properties, compared to films produced by continuous DC processing. More recently, interest has also focused on the effects which can arise when pulsed DC power is applied to the substrate. Pulsing the bias voltage appears to significantly increase the substrate ion current. For example, when compared to DC biasing, preliminary results have shown that a three-fold increase can be achieved in the current drawn at the substrate if the bias voltage is pulsed at 350kHz. However, despite these successes, aspects of this technology are not yet well understood. Consequently, detailed studies of the application of pulsed DC power, both to the magnetron and to the substrate, in a dual, variable field strength closed-field unbalanced magnetron sputtering system, are now in progress. Initial findings are reported here.

10:40am **TF-ThM8 Art and Science of Fabricating Optical Coatings by PECVD***, **L. Martinu**,* Ecole Polytechnique, Canada*; D. Poitras,* National Research Council of Canada, Canada **INVITED**

Low pressure plasma deposition using gas phase precursors is being increasingly used for the fabrication of dielectric optical films and coatings. This includes single-layer, multilayer, graded index and nanocomposite optical thin film systems for applications such as optical filters, antireflective coatings, optical waveguides and others. Besides their optical properties (refractive index, extinction coefficient, optical loss), these systems very frequently offer other desirable "functional" characteristics such as hardness, scratch-, abrasion- and wear resistance, adhesion to various technologically important substrate materials such as polymers, hydrophobicity or hydrophilicity, long-term chemical, thermal and environmental stability, and others. In this presentation, we review advances in the development of plasma processes and plasma systems, in the synthesis of high- and low index optical thin film materials, and in the control of plasma-surface interactions leading to desired film microstructures. We particularly underline the specific aspects of PECVD which are different from other conventional techniques used for optical films; this includes in particular fabrication of graded index (inhomogeneous) layers, high deposition rate, control of interfaces, enhanced mechanical and other functional characteristics, and industrial scale-up.

11:20am **TF-ThM10 Inhomogeneous Optical Coatings Deposited by Plasma***, **D. Poitras,*** National Research Council, Canada*; L. Martinu,* Ecole Polytechnique, Canada

Inhomogeneous optical coatings with a refractive index continuously varying with thickness appear to offer several attractive features from both fundamental and application points of view: (1) Understanding how accidentally-generated inhomogeneities can affect the optical performance of coatings can help to optimize the performance of optical filters; (2) purposely introduced and controlled optical inhomogeneities can be used to fabricate high performance inhomogeneous optical systems such as rugate filters; and (3) coatings with graded interfaces generally exhibit higher mechanical strength, better adhesion and good long term stability. In the present work, we studied these different aspects of inhomogeneous coatings produced by plasma enhanced chemical vapor deposition (PECVD). We used admittance diagrams (i) to interpret recent results concerning the effect of transition layers on the reflectance spectra of homogeneous single films, and (ii) to derive an alternative explanation of specific properties of rugate filters. In addition, we describe a simple way for introducing the refractive index dispersion while designing rugate filters. The latter approach is documented by the performance analysis of complex refractive index profiles in a double band rugate filter and in a chirp mirror fabricated by PECVD.

11:40am **TF-ThM11 Uranium Coated Optics for Space Applications in the Extreme Ultraviolet***, **D.D. Allred,** R.T. Turley,* Brigham Young University*; W.C. Cash,* University of Colorado*; M.B. Squires, D. Oliphant,* Brigham Young University

We have developed a new family EUV multilayer mirror coatings using uranium. Using this approach we have coated a set of 6 mirrors for the EUV Imager, a component of the IMAGE mission. It will study the distribution of He + in the Earth's plasmasphere by detecting its resonantly scattered emission at 30.4 nm (41 eV). The 30.4 nm feature is, in principle, relatively easy to measure because it is the brightest ion emission in the plasmasphere, it is spectrally isolated and the background at that wavelength is negligible. There is, however, a bright emission at 58.4 nm (21 eV) light, which comes from neutral helium in the earth's ionosphere which also must be blocked. It is at too high an energy to filter with aluminum but at too low an energy to have negligible reflectance from most materials commonly used in EUV mirrors. Thus, a multilayer system which satisfied two optical functions: high reflectance (>20%) at 41 eV but low reflectance (

Vacuum Technology
Room 201 - Session VT-ThM
Pumps and Large Vacuum Systems

Moderator: J.C. Helmer, AVS Fellow

8:20am **VT-ThM1 Design, Construction and Maintenance of Large Vacuum Systems***, **K.M. Welch**,* Consultant **INVITED**

Most good vacuum technicians know how to define the sources and sinks in large systems. We are conversant in gauging, pumps, flanges and seals, valves, leak detection, control systems, etc. We understand gas desorption mechanisms, beam scattering phenomena, the properties on a variety of esoteric materials, and other such art forms of our trade. This technical competence is necessary, but not sufficient for successful project execution. The keystone to the successful execution of any project resides in the planning, the planning methodology, and then the effective communication of that plan to facilitate coordination and engender cooperation. This seems rather mundane. But, it is truly the management challenge of any major project. Planning must be made with insight to the technical, fiscal, temporal, safety, and human relations components of the project. We must effectively communicate with management, sponsoring agencies, project organizations, service groups, staff, and with vendors. Most of Deming's 14 quality assurance tenants relate to creating an enlightened environment of good communications. All projects progress along six distinct, closely coupled, phases. The six phases are in a state of perpetual change. These project phases and their elements are discussed, along with a few management tools which have proven of value in the planning and execution of major projects.

9:00am **VT-ThM3 Design of the US Spallation Neutron Source Ring Vacuum Systems*, H.C. Hseuh,*** Brookhaven National Laboratory*; M. Mapes,* Brookhaven National Laboratory, usa*; D Pate, L. Smart, J. Tang, R. Todd, D. Weiss,* Brookhaven National Laboratory

Brookhaven is undertaking the design, construction and commissioning of the accumulator ring and the beam transport lines for the 1 GeV US Spallation Neutron Source. A vacuum of 1x10@super -9@ Torr or less is required in the ring to minimize the beam-residual gas ionization. All internal surface of the ring vacuum chamber walls will be coated with TiN to minimize the secondary electron yields thus avoiding the potential mulit-pactoring and e-p instability observed at some proton and positron storage rings. The layout of the ring and transport line vacuum systems, the design of the vacuum chambers, vacuum pumps and other hardware are presented. The calculated pressure distribution in the ring and the transport lines will be given. Development of the TiN coating process will be described. The architecture of the vacuum instrumentation and controls based on serial network links, PLCs and EPICS will also be presented. *Work performed under the auspices of the U.S. Department of Energy.

9:20am **VT-ThM4 The Interesting and Important Problem of Water in Vacuum Systems*, H.F. Dylla,*** Jefferson Lab **INVITED**

The author will review the phenomenology of water adsorption/desorption in vacuum systems. A review of the literature of outgassing shows that for unbaked metals, the outgassing is dominated by water, and the outgassing rate (Q) obeys a power law of the form Q = Q0 t -a, where a is near unity. A series of outgassing measurements@footnote 1@ have been performed on well characterized stainless steel surfaces which show that the outgassing power law exponent can vary from a = 0.7 - a = 1.2 as the metal surface is exposed from extremely dry N2 to increasing partial pressures of H2O. Relatively simple engineering formulae exist which quantify the amount of adsorbed/desorbed H2O as a function of exposure pressure, time and temperature. Models have been developed consistent with these data which invoke the oxide layer as the source volume for the outgassing and assume that the outgassing rate is limited by diffusion from the near surface region. Alternative models for outgassing of water have been described which assume surface desorption as the only source term.@footnote 2@ The author will discuss the additional measurements and modeling that are needed to achieve a more sophisticated understanding of water outgassing from metal surfaces. This work supported by US DOE Contract No. DE. @FootnoteText@ @footnote (1)@ Minxu Li and H.F. Dylla, J. Vac. Sci. Technol. A11, 1702 (1993); A12, 1772 (1994); A13, 1872 (1995). @footnote (2)@ P.A. Redhead, J. Vac. Sci. Technol. A, 13, 467 (1995).

10:00am **VT-ThM6 Large Motion Feedthrough Designs for Ultra Accurate Positioning in Vacuum*, T. Bisschops,*** Philips Research, The Netherlands

In the near future machining of special materials or substrates and e.g. semiconductor lithography will require an ultra clean gaseous or vacuum atmosphere. Large workpieces or substrates will need to be positioned at high speed (e.g. 20 m/s) with high acceleration (e.g. 2 g) and high accuracy (e.g. 5 nm). For industrial heavy duty applications large, differentially pumped, motion feedthrough designs have been developed. Feedthrough designs that allow for long stroke (e.g. 0.5 m) X, Y, Z, phi, theta positioning with high accuracy and for vacuum applications in the 10e-6 to 10e-8 mbar range will be presented.

10:20am **VT-ThM7 Design and Operation of Scroll Type Dry Primary Vacuum Pumps*, A. Liepert,*** *P. Lessard,* Varian Vacuum Technologies

Since being rediscovered two decades ago, scroll technology has been successfully adapted to vacuum use. Several innovations have allowed scroll-type pumps to produce vacuums lower than 10 mtorr; the pumps are used in many applications requiring an inexpensive, dry, long-lived pump. In this article, we detail the scroll design procedure, focussing on the tradeoffs between the need for sufficient vacuum and low manufacturing cost. In particular, the bearing and axial seal design are detailed. As an illustrative example, we consider the design requirements for a high helium compression scroll design for use in leak detectors. We also present guidelines for proper pump operation, including the need for gas ballasting, limits on high pressure operation and proper pump isolation schemes.

10:40am **VT-ThM8 Influence of the Production Parameters on the Vacuum Properties of Ti-Zr-V Non-evaporable Getter Films***, C. Benvenuti,* ***P. Chiggiato****, S. Clair, J.B. Clark, P. Costa Pinto, A. Escudeiro Santana, V. Ruzinov, I. Wevers,* CERN, Switzerland

Non-evaporable thin film getters of various composition have been produced by sputtering. Among the about 20 materials which have been studied, the lowest activation temperature (about 180°C) has been displayed by a Ti-Zr-V coating obtained from a cathode made of intertwisted elemental wires. In order to optimise the vacuum properties of this coating, the production parameters have been varied, namely sputtering configuration (diode or magnetron), discharge gas, deposition rate, discharge voltage, substrate nature and temperature during coating. The films have been analysed by electron microscopy, electron stimulated desorption, ultimate pressure, pumping speed and rare gas degassing rate measurements. The results are presented and discussed.

11:00am **VT-ThM9 Influence of the Elemental Composition and Crystal Structure on the Vacuum Properties of Ti-Zr-V Non-evaporable Getter Films***, C. Benvenuti, P. Chiggiato, A. Mongelluzzo,* ***A. Prodromides****, V. Ruzinov, M. Taborelli,* CERN, Switzerland*; F. Lévy,* EPFL, Switzerland

Non-evaporable thin film getters of various composition have been deposited by sputtering. Among the 20 materials that have been studied, the coating with the lowest activation temperature (about 180 °C) has been found in the Ti-Zr-V system sputter-deposited from a cathode made of intertwisted wires of the constituent elements. In an attempt to reduce the activation temperature, Ti-Zr-V films of various composition have been deposited by means of a dedicated three-cathode planar magnetron sputtering configuration, and then characterised by Auger electron spectroscopy and pumping speed measurements. We have found that the lowest activation temperatures and the highest pumping speeds are obtained only in a confined zone of the Ti-Zr-V system, corresponding to an amorphous or nanocrystalline structure. Important and irreversible reductions of the getter film pumping speed are observed when the film structure is modified by heating.

11:20am **VT-ThM10 Miniature Vacuum Pumps*, J.W. Weed*[1]***, Sandia National Laboratories **INVITED**

Miniature analytical instruments that operate in a rarified gas environment will require vacuum pumping systems that are of suitable performance, size, weight, and power consumption. A subset of these analytical instruments will require throughput pumping systems, that is systems that exhaust pumped gas to the external environment rather than capturing it. Vacuum pumps are available in both capture and throughput configurations. Most "normal" sized gas analytical systems in use today are equipped with throughput pumping systems because of sampling and total mass flow requirements. This talk will describe existing pumps and efforts to miniaturize them. Performance and design criteria will be explored focusing on creating specifications based on overall system requirements. Problems with shrinking existing designs as well as several novel designs will be considered. Some new microfabrication processes will be described with an eye towards techniques that will be helpful in the fabrication of miniature vacuum pumping systems. *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.

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[1] **Featured Speaker - Science and Technology in the 21st Century**

Biomaterial Interfaces
Room 202 - Session BI+NS-ThA

Biosensors

Moderator: A. Chilkoti, Duke University

2:00pm **BI+NS-ThA1 Substrate and Attachment Chemistry Effects on Adsorption and Single-Base Mismatch Discrimination on Immobilized Oligonucleotide Arrays***, **J.E. Forman**, L. Gamble, R.S. Gascon, J.I. Henderson, A.D. Suseno, P. Wagner,* Zyomyx, Inc. **INVITED**

Hybridization efficiency and ability to discriminate between perfect match and single-base mismatch target sequences are fundamental to performance of arrays of covalently immobilized nucleic acids (probes). Two factors that significantly contribute to array performance are density and orientation of immobilized probes. Probe density not only controls how much bound target is adsorbed, but also affects the kinetics and thermodynamics of duplex formation. Perturbations to duplex formation occur when the spacing of probes is close enough to force inter-probe association and crowding, phenomena that interfere with target sequence adsorption. However, these perturbations can induce beneficial effects in array performance. For example, crowded nucleic acid surfaces demonstrate lower apparent melting temperatures (T@sub m@'s) than the solution phase, but also show discrimination between matched and mismatched sequences under low stringency conditions. The orientation of the probe is highly dependent on the method of immobilization to the surface. Non-optimal attachment can orient the probe in a way that interferes with duplex formation, or such that it becomes buried within the surface and inaccessible to the target sequence. The substrate used for array preparation ultimately controls both density and orientation; optimization of the substrate can enhance array performance in an assay. Especially interesting is a precise control of probe density, where the density effects alter the T@sub m@'s of immobilized sequences to allow a broad range of sequence to be analyzed in a single temperature assay. We have been exploring a variety of silane modified substrates for the preparation of oligonucleotide arrays, focusing on immobilization of the probe through amine or thiol moieties. The effect of density and attachment chemistry on target adsorption and single-base mismatch discrimination with single and double stranded oligonucleotide target sequences will be presented.

2:40pm **BI+NS-ThA3 Investigation of DNA Hybridization on Surfaces by Surface Plasmon Fluorescence Spectroscopy (SPFS)***, **T. Neumann**, W. Knoll,* Max-Planck Institute for Polymer Research, Germany

The investigation of DNA hybridization on surfaces, and as a consequence, the development of DNA-chips and sensors, has been of increasing interest in recent years, since such technology can be used to investigate the human genome. We report here a study of PNA:DNA and DNA:DNA hybridization on surfaces measured by surface plasmon resonance spectroscopy (SPS) coupled with fluorescence (SPFS) and surface plasmon microscopy (SPM). PNA (peptide nucleic acids) and DNA catchers were immobilized either directly on gold surfaces by thiol linkers or via biotin on streptavidin covered gold surfaces. In order to enhance the detection limit of the SPR, the fluorescence signal of dyes attached to the target strands was detected during the hybridization to the immobilized catchers. To get a deeper insight into the underlying principles of the hybridization process near surfaces, conformational changes in the catcher and target DNA structure were monitored by comparing the hybridization kinetics obtained by having the fluorescent dye attached either to the catcher or the target and varying the length of both types of strands. Furthermore by using two different fluorescent dyes on the DNA strands, we were able to carry out Forster transfer experiments during the hybridization step, which allowed us to monitor distance changes between the catcher and target at the surface.

3:00pm **BI+NS-ThA4 Fluorescence Detection of Surface DNA Hybridization Reactions Based on Surface Structural Changes***, **T.H. Huang**, S.J. Stranick, M.J. Tarlov,* National Institute of Standards and Technology

We describe a novel fluorescence method for the detection of surface-immobilized DNA hybridization reactions. Solid phase hybridization reactions form the basis of DNA chip technologies that are used for sequencing and genetic diagnostic applications. In conventional fluorescence-based detection schemes, the "target" DNA is typically labeled with a fluorophore. We report a method where instead, the "probe" DNA is labeled with a fluorophore. Our model surface hybridization system uses a mixed monolayer of fluorescein-tagged, thiol-derivatized, single-stranded DNA probes and 6-mercaptohexanol self-assembled on Au surfaces. Prior to hybridization, the fluorophore on the probe is in closer proximity to the gold surface, resulting in greater quenching of the fluorescence signal. Upon hybridization, the double-stranded DNA adopts a rod-like structure that extends the fluorophore away from the gold surface. With the fluorphores located further from the gold surface, quenching is reduced and an increase in fluorescence intensity is observed. Parameters affecting fluorescence intensity such as probe surface coverage, probe length, and target concentration will be discussed. In addition, a comparison of probe- and target-labeled fluorescence detection schemes will be made.

3:20pm **BI+NS-ThA5 Silicon Surface Chemistry for DNA Immobilization***, T. Strother, Z. Lin, W. Cai, L.M. Smith, **R.J. Hamers**,* University of Wisconsin, Madison

Many emerging areas of biotechnology, such as "gene chips", seek to leverage many aspects of the existing infrastructure in microelectronics and apply it to new areas. While most previous work has focused on the attachment of DNA to surfaces of gold or glass, we have investigated the chemistry involved in covalently bonding DNA to Si(001) and Si(111) surfaces in a way that retains its ability to selectively hybridize with its solution-phase complements. The use of XPS to study the chemical structure at each step in the DNA attachment process has lead to the development of new procedures that are both simple and robust. Starting with hydrogen-terminated Si(001) and Si(111) surfaces, photochemical excitation at 254 is used to remove the photo-labile hydrogen; the exposed surface is then reactive toward organic molecules containing one or more unsaturated C=C bonds. "Linker" molecules containing a C=C double bond with another functional group(such as an amine or ester group) are then used to provide a dense set of surface-bound functional groups for attachment of DNA. To control the selectivity of the attachment process, however, careful optimization of the molecular structure of the linker and the other processing conditions are required. The density and chemical uniformity of the surface (as judged by XPS) is highly correlated with the intensity and selectivity achieved in subsequent binding of the surface-bound DNA to its fluorescently-labeled complements in solution. The results show that control of surface chemistry indeeds leads to significant improvements in the formation of DNA-functionalized silicon surfaces.

3:40pm **BI+NS-ThA6 BARC: A Magnetoresistive Biosensor@footnote 1@***, **P.E. Sheehan**,* Naval Research Laboratory*; R.L. Edelstein,* Geo-Centers, Inc.*; C.R. Tamanaha, M. Miller,* Naval Research Laboratory*; L. Zhong,* Geo-Centers, Inc.*; R.J. Colton, L.J. Whitman,* Naval Research Laboratory

The Bead ARray Counter (BARC) is a revolutionary biosensor that uses DNA microarrays, magnetic microbeads, and giant magnetoresistive (GMR) magnetic field sensors to detect and identify biological molecules.@footnote 2@ The current prototype is a table-top instrument with integrated fluidics under development for the detection of biological warfare agents. The core of the sensor is a small, microfabricated chip containing a GMR sensor array for detection of up to eight different pathogens. Oligonucleotide probes complementary to pathogen target sequences are arrayed onto the microfabricated chip directly above the GMR sensors. Specific hybridization is measured and discriminated from non-specific background by addition of functionalized magnetic microbeads that bind to the captured target DNA. The beads tethered to the surface are detected by the GMR sensors, with the intensity and location of the signal indicating the concentration and identity of the target pathogens. A complete assay, including hybridization and detection can be performed in approximately 30 min. Because each GMR sensor is capable of detecting a single magnetic bead, in theory, the BARC biosensor should be capable of detecting a single molecule. With recent advances in GMR technology for computer memory, chips with millions of sensors will soon be commercially available, enabling the development of a BARC sensor capable of detecting thousands of analytes simultaneously. We will discuss the scientific and technical challenges to making such a sensor system a reality. @FootnoteText@ @footnote 1@Supported by the Defense Advanced Research Projects Agency. @footnote 2@Edelstein et al., Biosensors & Bioelectronics 14, 805 (2000).

4:00pm **BI+NS-ThA7 A Biosensor Based on Force Differentiation@footnote 1@***, **C. Yanavich**, M. Malito,* Nova Research, Inc.*; G.U. Lee, L.J. Whitman, R.J. Colton,* Naval Research Laboratory*; M. Natesan,* Geo-Centers, Inc.

We are developing an array biosensor that uses a magnetic force to differentiate specific ligand-receptor binding from non-specific ligand-surface binding. In this force differentiation assay biosensor, capture antibodies that will bind to specific target analytes within a sample are first coated onto a surface. The captured analyte is then sandwiched by a second antibody that is attached to a magnetic microbead. A magnetic force with well-defined magnitude and orientation is applied to remove the non-specifically adsorbed beads, and a semi-automated optical reader then measures the number of the specifically bound beads remaining on the surface (which can be correlated with the analyte concentration). The original prototype used polystyrene microtitre wells for multi-analyte detection. We are now developing a second-generation sensor that employs a filter membrane as the capture surface. The filter facilitates concentration of the antigen on the surface and enhances the antigen-antibody interactions, significantly reducing the assay time (to ~30 min), and increasing the sensitivity by two-to-three orders of magnitude. Several techniques are being investigated to pattern capture antibodies onto the filter surface in order to enable multi-analyte detection on a single disposable filter. They include photo patterning with photo-activated biotin or caged photo-biotin, and imprinting via PDMS masks. We will also discuss our development of alternate techniques aimed at simplifying the bead counting system. @FootnoteText@ @footnote 1@Supported by the Joint Service Technical Panel for Chemical and Biological Defense (JSTPCBD).

4:20pm **BI+NS-ThA8 Encapsulation of Smart Polymers in Silica: Stimuli-Responsive Porous Hybrid Materials That Incorporate Molecular Nano-Valves***, G.V. Rama Rao,* ***G.P. Lopez,*** University of New Mexico*; A. Chilkoti,* Duke University

Elastin (a protein) and poly(N-isopropyl acrylamide) (PNIPAAM, a synthetic polymer) are two types of thermo-sensitive, smart polymers which exhibit inverse solubility in water upon heating and undergo the transition from hydrophilic conformations to hydr ophobic conformations at a temperature known as lower critical solution temperature (LCST). This interesting property has led to have several applications in biotechnological areas. In this report, we describe the development of molecular switches as nan os copic actuators that can control the transport of chemical species by encapsulating PNIPAAM and elastin in dense silica gels by sol-gel synthesis. Cycling through the LCST can control molecular permeability through these hybrid materials. The pores res ult ing from the transition can selectively transport molecular species depending on their size. For example, permeation experiments revealed the LCST behavior of PNIPAAM in silica-polymer membranes and was identified to be 31 °C. DSC studies on bu lk gels are in good agreement with the permeation results. Cycling of the membranes between 25 and 40 °C indicates the membranes possess reversible, variable permeability while maintaining good mechanical stability. Importantly, permeation experiments on PNIPAAM-si lica membranes with various molecular weights of poly(ethylene glycol) have clearly demonstrated that the membrane is acting as a molecular switch by being impermeable below the LCST, and permeating the lower molecular weights of poly(ethylene glycol) and filtering out higher molecular weight polymers above LCST.

4:40pm **BI+NS-ThA9 Adsorption Behavior and Optical Properties of Surface-Adsorbed Polystyrene Nano Particles***,* ***M. Himmelhaus,*** Universität Heidelberg, Germany*; H. Takei,* Hitachi Central Research Laboratory, Japan

Polystyrene (PS) nano particles have become popular tools in photonics, nano technology, and life science since they have become commercially available in a wide range of sizes with narrow size distribution. While most applications utilizing surface-adsorbed PS nano particles deal with ordered arrays on mesoscopic scale, recently a chemically induced method for adsorption of such particles was introduced to yield random-close-packed (rcp) monolayers of almost arbitrary lateral extension. Such layers can be used as a template for the formation of cap-shaped Gold nano particles that exhibit extraordinary optical properties@footnote 1@ and thus can be developed into a sensitive optical biosensor.@footnote 2@ Here we demonstrate that the chemically induced adsorption method can be combined with alkanethiol chemistry to gain better control of sphere adsorption. Thus, sphere layers of varying density can be fabricated and their optical properties can be studied as a function of coverage. By further utilizing Micro Contact Printing (µCP) of tailgroup modified alkanethiols 2D patterns of rcp PS sphere monolayers with a lateral resolution of a few microns and a total pattern area of ~1 cm@super 2@ can be produced. These patterns are a first step to the development of an optical biosensor based on cap-shaped Gold nano particles with massively parallel detection capability. @FootnoteText@ @footnote 1@ H. Takei, J. Vac. Sci. Technol. B 17 (5) 1906, 1999 @footnote 2@ M. Himmelhaus, H. Takei, Sens. Acuators B 63 (1-2) 24, 2000

5:00pm **BI+NS-ThA10 Formation and Patterning of Supported Fluid Lipid Bilayers on a High Refractive Index Substrate***,* ***C.M. Ajo,*** *L.C. Kam, S.G. Boxer,* Stanford University

Supported lipid bilayers are a useful model system to probe cellular membrane components and their interactions in a near native environment. Specifically, membrane components reconstituted in supported lipid bilayers create a well-defined two-dimensional system that can be manipulated - and then interrogated with a variety of surface specific and optical techniques. Several of these techniques rely on evanescent fields to probe the region near the solid support-lipid bilayer interface. However, the solid support typically has been a low refractive index material that permits the evanescent wave to penetrate significantly beyond the bilayer (650 Å). Here we report the formation of supported lipid bilayers on lithium niobate (LiNbO@sub 3@), a material with a high refractive index (n=2.3). Vesicle fusion onto lithium niobate forms a single uniform supported lipid bilayer that exhibits lateral diffusion properties similar to glass-supported lipid bilayers. By blotting and stamping,@footnote 1@ supported bilayers can be patterned reversibly, and the lipid components reorganize in response to an electric field. The high refractive index of lithium niobate restricts the penetration of an evanescent field to within 160 Å of the solid support-lipid bilayer interface. This provides a method to study the cell-supported lipid bilayer interface, since the relevant distances are on this order. Additionally, the transparency of lithium niobate ove a wide range of wavelengths makes it a useful substrate for both visible and infrared studies. @FootnoteText@ @footnote 1@J. S. Hovis and S. G. Boxer, Langmuir 16, 894 (2000).

Dielectrics
Room 312 - Session DI+EL+MS-ThA
High K Dielectrics: Perovskites

Moderator: J.N. Kidder, University of Maryland

2:00pm **DI+EL+MS-ThA1 High Density Thin Film Ferroelectric Nonvolatile Memories***,* ***R. Ramesh,*** University of Maryland **INVITED**

Over the past two years, we have focused considerable effort on understanding the deposition and characterization of conducting barrier layers for the direct integration of ferroelectric capacitors on a poly-Si plug. Our specific focus has been on the materials science of the barrier layers to understand the role of crystallinity and process parameters on the structural and chemical integrity of the barrier layers during the subsequent growth of the ferroelectric capacitor stack. We are using the PZT system with conducting oxide electrodes as a prototypical test system for which at least two different conducting barrier materials systems have been successfully developed. Using both epitaxial and polycrystalline capacitors on these conducting barriers as test vehicles, we have been carrying out systematic studies on the effect of composition, point defect chemistry, strain and other processing variables on the structural integrity and ferroelectric properties. A novel aspect of our work is the use of scanning electric force microscopy techniques to understand the microscopic influence of film microstructure on the ferroelectric properties. In this presentation, we will present results of our progress on the process integration, device properties, specifically, polarization switching and relaxation dynamics and microscopic observations of ferroelectric properties and time dependent changes ; stress effects on fundamental properties.This work is supported by the NSF-MRSEC under Grant No. DMR- 96-32521 and by Bellcore.

2:40pm **DI+EL+MS-ThA3 Process Window Extension of TiN Diffusion Barrier using Pre-oxidation of Ru and RuO@sub x@ Film for (Ba,Sr)TiO@sub 3@ Dielectric Film***, H.J. Kim, S. Kim,* Hyundai Electronics Industries Co. Ltd., Korea

(Ba,Sr)TiO@sub 3@(BST) thin film and other high dielectric oxides have attracted considerable attention due to their possible application in dynamic random access memories. However, serious integration issues are faced with in many cases because BST films need to be grown at rather high deposition or post-annealing temperatures of above 600°C in an oxidizing ambient. Deterioration of capacitor performance may result from interdiffusion and oxidation. Therefore, a diffusion barrier for oxygen should be developed for high-density DRAM device. In order to extend the process window of conventional sputtered TiN diffusion barrier and find out a proper electrode, in this experiment, the effect of pre-annealing method on the oxidation behavior of TiN barrier during 2 step annealing for BST dielectric film. Rapid thermal annealing in oxygen ambient (RTO) and N@sub 2@O plasma oxidation was respectively introduced to form a thin

RuO@sub x@ layer and bind between oxygen and Ru at the surface of each Ru and RuO@sub x@ film. It is expected that a thin RuO@sub x@ layer be formed at the surface of each film by RTO and N@sub 2@O plasma. This can be retarded the oxygen indiffusion through Ru and RuO@sub x@ layer at high temperature due to complex diffusion paths and strongly stuffed along the grain boundaries as well as matrix. Two steps annealing for BST dielectric film is recently introduced to minimize the oxidation of diffusion barrier. In this work, a role of thin RuO@sub x@ oxidized layer formed at the surface of each Ru and RuO@sub x@ film by different pre-annealing methods prepared with/without BST deposition is investigated during two steps annealing.

3:00pm **DI+EL+MS-ThA4 Atomic Polarization and Screening Charge by Variable Temperature Scanning Probe Microscopy of Ferroelectric Surfaces*, S.V. Kalinin,* *D.A. Bonnell,* University of Pennsylvania**

Atomic force microscopy (AFM), electrostatic force microscopy (EFM), scanning surface potential microscopy (SSPM) and piezoresponse imaging (PRI) are applied to the BaTiO3 (100) phase transition. The imaging mechanism for non-contact microscopies (EFM and SSPM) based on an analytical solution for potential and field above the surface is discussed. The PRI imaging mechanism on a ferroelectric surface is analyzed in terms of the solution of the combined electrostatic-piezoelectric indentation problem. The relationship between SPM signal and screened and unscreened charge density is established. Quantification of force and force gradient-distance dependencies indicate that polarization bound charge is screened on this surface when imaged in ambient environments. The absolute value of the measured potential difference between domains of opposite polarity suggests that surface adsorbates play the governing role in surface potential. This conclusion is corroborated by a direct measurement of the phase transition and by observations of domain wall motion. The influence of tip shape effects and mobile surface charges on effective domain wall width is also discussed. The contribution of electrostatic forces to piezoresponse contrast is extracted from force-distance measurements and its influence of the local hysteresis loops is estimated. Considerations regarding the polarization switching by the tip are presented. Based on the experimental observations for this and other systems the dominant role of electromechanical vs. electrostatic effects in PRI imaging mechanism is established.

3:20pm **DI+EL+MS-ThA5 Film-formation Mechanisms, Microstructure, and Properties of BST Thin Films Grown By MOCVD*, Y. Gao,*** Pacific Northwest National Laboratory **INVITED**

A review of MOCVD BST thin films will be presented, focusing on precursor chemistry, film-formation mechanisms, and relationship between film processing, microstructure and dielectric properties. In particular, the precursor chemistry and film-formation r eactions have been studied using isotopic labeling experiments (@super 18@O@sub 2@). The precursor chemistry was found to strongly depend on substrate materials. In an oxygen ambient, at least four different reaction processes involved the removal of carb on from the precursor ligands on oxide covered Pt(111). Time-of-flight secondary ion mass spectrometry reveals both M@super 18@O and M@super 16@O (M= Ba, Sr, Ti) in the BST films, indicating that the oxygen in the BST films originates from both the gas ph ase oxidants (@super 18@O), and the precursor ligands (@super 16@O). The ligand substitution by gas phase O@sub 2@ plays a more prominent role in the film-formation at lower temperatures. On the other hand, the reactive oxygen radicals produced by micr owave plasma involved more in breaking the O-C bonds than substituting the precursor ligands for the film formation, resulting in larger surface roughness. Use of the 50%@super 18@O@sub 2@-50%N@sub 2@@super 16@O mixture results in a reduction of @super 18@O incorporation in the BST films, indicative of the direct involvement of N@sub 2@O in the film-formation reactions. The mechanistic studies are essential for understanding the BST precursor properties, and provide useful information to correlate the fil m m icrostructure, step coverage, and dielectric properties with the precursor properties. In addition, the study shows that precursor reactivities strongly affect the step coverage on the 3D structure, but little effect on the microstructure, surface morphology, and dielectric properties of the stoichiometric BST films. These properties strongly depend on the film composition, substrate material, and growth temperature.

4:00pm **DI+EL+MS-ThA7 Epitaxial (Ba,Sr)TiO@sub 3@ on MgO for Room Temperature Microwave Phase Shifters*, C.L. Chen,*** *J. Shen, S.Y. Chen, C.W. Chu,* University of Houston*; F.W. Van Keuls, F. Miranda,* NASA Glenn Research Center*; J.C. Jiang,* Louisiana State University

Single crystalline ferroelectric Ba@sub 0.6@Sr@sub 0.4@TiO@sub 3@ thin films were epitaxially grown on (001) MgO by using pulsed laser ablation. Microstructure studies from x-ray diffraction and electron microscopy suggest that the as-grown films are c-axis oriented with their interface relationship of @sub BSTO@//@sub MO@. Edge dislocations were found through the entire interface in every 8 unit cell length. Microwave property measurements indicated that the room temperature coupled microwave phase shifter have achieved with phase shift over 200@super o@ at 23.675 GHz and a figure of Merit of about 55@super o@/dB. The room temperature dielectric constant and loss tangent were found to be 1688 and 0.008 and the tunability was 33% with 2.5V/µm. The result suggests that the performance of microwave phase shifter based on the epitaxial ferroelectric thin films on (001) MgO are closed to the practical applications in the wireless rf communications.

4:20pm **DI+EL+MS-ThA8 High Temperature Etch Processing for FeRAM MFM Capacitor Stack Fabrication*, L.G. Jerde,*** *A. Cofer, R.A. Ditizio, S. Marks, J.A. Meyer, K.A. Olson, S.P. DeOrnellas,* Tegal Corporation

The unique materials utilized in FeRAM MFM capacitor stacks present numerous integrated device fabrication challenges, particularly in the patterning of these materials and the capacitor stacks that utilize them. Many of these patterning challenges are due to the intrinsic involatility of the reaction products formed when etching the elemental constituents of the FeRAM materials (i.e., Pt, Ir, Pb, Zr, Sr and Bi). These challenges have been successfully met for several years by utilizing photoresist etch masks in conjunction with the plasma etch technologies of low pressure, high density and dual frequency. While this technological approach is extendible for the foreseeable future of FeRAM capacitor stack definition, the intrinsic involatility of their etch reaction products has recently sparked wide spread interest in utilizing high temperature etch processes to meet the as yet undefined future requirements for these applications. Although there are benefits to this high temperature approach, there are also risks. Among these risks are a number of key considerations that must be dealt with to successfully develop and implement high temperature etch process solutions for FeRAM applications. The first set of these considerations is related to the requirement that the etch tool provides reliable wafer, as opposed to wafer chuck, temperature and temperature uniformity control. In view of the industry trend toward single mask, full stack processes, another set of considerations is the requirement that the etch tool be able to rapidly vary the wafer temperature to accommodate the optimum temperature for each of the FeRAM materials being used. Yet another set of considerations are those related to wafer temperature limitations imposed by the Perovskite structure transition temperature, device damage and thermal budget. We will discuss and illustrate these considerations and present selected high temperature etch process results for various FeRAM films and stacks.

Material Characterization
Room 207 - Session MC-ThA

Evolving Technologies in Surface Analysis

Moderator: E. Garfunkel, Rutgers University

2:00pm **MC-ThA1 In-situ Control of Wet Chemical Etching of Patterned Bulk-GaAs using Real Time Spectroscopic Ellipsometry*, S.-J. Cho,*** *P.G. Snyder,* University of Nebraska, Lincoln*; C.M. Herzinger, B. Johs,* J. A. Woollam Co.

High controllability and reproducibility of the etching process are regarded as key factors for the success of device fabrication. In-situ optical techniques such as real time spectroscopic ellipsometry (RTSE) may be used to control etch depth as well as determine etch rates. We have previously demonstrated control of etch depth through the cap and AlGaAs layers of an unpatterned GaAs/AlGaAs/GaAs heterostructure. In this work, in-situ monitoring and control of etch depth in patterned bulk GaAs was studied using RTSE. Patterning is necessary for monitoring etching in the bulk substrate (unlike etching in thin layers), since without it optical interference would not occur. Patterned (lines or squares) pieces of bulk GaAs wafer were etched in a citric acid-hydrogen peroxide-deionized water etch solution. The grating periods were 10, 20, or 40 µm. During the etching RTSE data were taken and simultaneously analyzed, and etching was stopped when the fitted etch depth reached a predetermined value (for example, 1.6 µm). The final etch depth was confirmed by ex-situ spectroscopic ellipsometry and SEM analyses. The etch rate of bulk GaAs was also determined based on the real time fit results. The model currently used for RTSE data analysis assumes spatial coherence of the light beam over an area large compared with the grating period, but does not explicitly include diffraction effects. This model appears to work well for grating periods in the range 20~40 µm. These and the previous results show that RTSE can be used to control etch depth in both thin layers and the substrate. Research supported by AFOSR Grant #49620-96-1-0480.

2:20pm **MC-ThA2 In- and Ex-situ Characterization by Second-harmonic Generation of the RPECVD Oxidation and Nitridation of Silicon and Ex-situ Comparisons with Other Optical Techniques*, G.D. Powell,*** *R.S. Johnson, G. Lucovsky, D.E. Aspnes,* North Carolina State University

We report azimuthal dependences of second-harmonic generation (SHG) spectra obtained in-situ and ex-situ from 800 to 900 nm of oxide, nitride, and oxynitride interfaces formed by Remote Plasma Enhanced Chemical Vapor Deposition (RPECVD) on singular and vicinal Si(111) substrates. Spectral dependences are linear over this limited spectral range that make it possible to compare slopes and intercepts among the different processes. SHG measurements were performed for both p-p and p-s polarization configurations. We found only slight variations for the terminations except for one parameter describing the electric field phase differences for the step for the nearest direction. We also observe significant differences, of the order of 10 meV, in ellipsometrically determined apparent critical point energies and broadening parameters under various processing conditions. Finally, we advance beyond a purely phenomenological model of a signal associated with the bond symmetries to a more physical model that directly connects the macroscopically measured far-field intensity to the dipole radiation from the anharmonic bonds.

2:40pm **MC-ThA3 What Is Needed and What Is Practically Available for Small Area, Small Depth, Chemistry Sensitive Analysis in the Semiconductor Wafer Processing Industry*, C.R. Brundle*** [1] *,* Applied Materials **INVITED**

The continuing health of the semiconductor industry depends on the insatiable demand to reduce CD (critical dimensions), eg gate length and thickness, interconnect line dimensions, barrier layer thickness. For needed analytical methods, this translates into improved spatial resolution (area and depth). In addition, because of (a) the drive towards where everything is interface, (b) the introduction of many "non-traditional" materials (eg Cu, low k, high k), and (c) a general push towards even higher yields, the need for chemical state information has increased and will continue to increase. In this paper I review, from a wafer processing perspective, what analytical instrumentation is needed, compared to what is actually available. I also try to define the differences in instrumentation needs for "analytical laboratory" usage and "metrology usage." Though I will concentrate on techniques which are thought of as surface sensitive (eg electron spectroscopies), there is no longer any practical reason to distinguish these from techniques which are not mainly thought of as surface sensitive (eg EDS, Raman). The reason is twofold. First, we need information over a range of depth. Second, such techniques can be, and have been, made more surface/interface/small area applicable than has been traditional. Finally, since our particular interests have to do with small particle defects during wafer processing, I will give examples to illustrate our current capabilities and our unmet needs.

3:20pm **MC-ThA5 Dopant-Induced Contrast of Si Devices in PEEM*, V.W. Ballarotto,*** *K. Siegrist, R.J. Phaneuf, E.D. Williams,* University of Maryland

Spatial variation of doping, such as in a pn junction, produces contrast in photoelectron emission microscopy (PEEM) that may be useful for dopant profiling, failure analysis, or as a processing diagnostic of Si. The contrast mechanism arises from reduction of the effective photothreshold when Si is heavily to degenerately doped. We report on a quantitative investigation of doping-induced contrast in PEEM images of Si devices. The calibration samples consist of p-type (B) stripes of different dopant concentrations and line separations, written on n-type (N@sub d@=10@super 14@ cm@super -3@) Si(001) substrates. Using a near-threshold light source, we find that the signal intensity increases monotonically with B concentration over a range of doping from 1x10@super 18@ to 6x10@super 20@ cm@super -3@. The measured intensity ratios are in good agreement with a calculation based on photoemission from the valence band. In addition, PEEM images of memory chip devices acquired through a 2000 Å SiO@sub 2@ layer and showing clear doping contrast will be shown. This depth sensitivity and the potential for improved doping contrast will be discussed in terms of the incident photon energy above threshold. This work is supported by Advance Research Development Activity (ARDA) grant number: 97-C-3048.

3:40pm **MC-ThA6 Elemental Mapping of Sub-µm Particles and Structures by LASER-SNMS and TOF-SIMS*, F. Kollmer,*** *R. Kamischke, R. Ostendorf,* Physikalisches Institut der Universitaet Muenster, Germany*; H. Bender,* Materials and Components Analysis Group IMEC*; A. Benninghoven,* Physikalisches Institut der Universitaet Muenster, Germany

Sputtering-based surface mass spectrometry as SIMS or Laser-SNMS combines high sensitivity with high lateral resolution, provided a high fraction of sputtered particles is ionized and a finely focused primary ion beam is applied. For sub-Âµm characterization the transformation probability of a surface atom into an ion should be optimized. The large fraction of sputtered neutrals and their efficient laser-postionization result in high Laser-SNMS sensitivities. The use of a time-of-flight (TOF) mass spectrometer guarantees parallel mass registration at high transmission. We report on recent results of TOF-SIMS and Laser-SNMS characterization of sub-µm particles. The analyzed particles include Al@sub 2@O@sub 3@, Fe@sub 2@O@sub 3@ and CeO@sub 2@ with diameters down to 15 nm. On the base of these results we compared both techniques one with the other and in addition with Scanning Auger Microscopy (SAM). The know how gained from these investigations was applied to supported metal catalysts and other sub-Âµm structures such as magnetic heads. By applying a combined TOF-SIMS/Laser-SNMS instrument, a direct comparison of both techniques was possible. The use of a 30 keV finely focused Ga@super +@ source and a time-of-flight instrument guarantees high lateral (@>=@80 nm) and mass resolution at high transmission. For nonresonant postionization an excimer-laser (193 and 248 nm) was applied. SAM characterization was carried out in a VG 350 F instrument. We determined useful yields, as a measure of sensitivity, for a variety of mono-elemental metal samples. The obtained useful yields in the order of 10@super -2@ (SNMS) and 10@super -3@ (SIMS) allow to analyze structures well below the spot size of the primary ion beam. We found higher elemental sensitivities for TOF-SIMS and especially Laser-SNMS compared to SAM. Quantification was possible by the use of SAM and Laser-SNMS, the latter additionally allows to estimate the total amount of material in a particle.

4:00pm **MC-ThA7 Dose Quantity Effects on Nano-scaled Dot Size and Depth Profile of Gallium Implantation on Silicon by Finely Focused Ion Beam*, L. Shen,*** *L.C. Feldman, R.F. Haglund Jr., R.A. Weller,* Vanderbilt University

In a FFIB(Finely Focused Ion Beam) System, the beam current is controlled by choosing the aperture, which determines the spot size on nano-materials fabrication. The total beam dose is determined by beam current intensity, beam duration time and scan repeat rate. The total dose determines the ultimate feature size. We have investigated the total dose effects on apparent spot size and depth profiles by controlling beam current intensity, beam dwell time and/or scan times. In particular we report the AFM apparent spot size for a single scan as a function of dwell time and compare to theoretical estimates. We also report apparent spot size as a function of number of scans. Achieving minimum spot size is critical for creating nano-scale feature size and depth profile.@footnote 1@ @FootnoteText@ @footnote 1@Supported in part by the National Science Foundation under grant DMR-9871234 and by the U.S. Army Research Office under contract DAAD-19-99-1-0283.

4:20pm **MC-ThA8 Ion Channeling Effects on the FIB Milling of Crystalline Materials*, B.W. Kempshall,*** *S.M. Schwarz,* University of Central Florida*; B.I. Prenitzer,* Lucent Technologies*; L.A. Giannuzzi,* University of Central Florida*; R.B. Irwin, F.A. Stevie,* Lucent Technologies

The focused ion beam (FIB) instrument is being used as a fundamental tool for the investigation of ion beam/material interactions. One particular topic of interest is the effects of ion channeling on the sputtering behavior of Si and Cu. Although applications involving the FIB milling of Si are straightforward, the FIB milling of Cu may be complicated by effects such as the development of milling induced topographical features. The difference in milling behavior between Si and Cu may be attributed to the inherent physical properties of materials that influence the sputtering yield. As ions channel deep into the target along preferred crystallographic directions, a corresponding decrease in sputtering yield is observed. In this presentation, the effects and the mechanism of Ga+ channeling in Cu is used to illustrate the relationship between the sputtering yield, the quality

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[1] **Featured Speaker - Science and Technology in the 21st Century**

of FIB mill cuts, and the surface characteristics of FIB milled Cu for various crystallographic orientations. The correlation between the theoretical Lindhard-Onderdelinden axial channeling model and the observed ion channeling contrast in the FIB milling of Cu is investigated.

4:40pm **MC-ThA9 XPS Analysis of Si Samples Prepared Using the FIB Lift-Out Technique*, A.C. Ferryman*,** *J.E. Fulghum,* Kent State University*; L.A. Giannuzzi,* University of Central Florida*; F.A. Stevie,* Cirent Semiconductor

Si samples prepared using the FIB lift-out technique were analyzed using high spatial resolution XPS imaging and spectroscopy. Sample mounting and associated problems with sample location will be discussed. The analyzed samples were 5 x 20 micron cross-sections mounted on carbon-coated TEM grids. Results indicate that XPS data can be acquired from FIB lift-out samples. XPS provides new information about the effect of Ga surface residue on the Si surface.

5:00pm **MC-ThA10 Determining Area Selectivity in Small-Area XPS Analysis@footnote 1@*, D.R. Baer,*** *M.H. Engelhard,* Pacific Northwest National Laboratory

For many real world applications, the ability of new XPS instrumentation to examine small features can be a tremendous advantage. Most users and vendors define the spatial resolution of these instruments in a similar relatively simple and useful fashion involving resolution of a sharply defined edge or grid. However, it can be useful and is sometimes important to know the area of a sample that actually contributes to the XPS spectra measured. We have found that measurements on well defined "dots" of a material on a substrate provide a useful experimental approach for determining the area of a specimen that contributes to a small area XPS measurement. The method provides a way to verify instrument operation and set up conditions and the adequacy of specimen alignment procedures for small area analysis. Data collected from a Phi Quantum 2000 and a Kratos Axis 165 demonstrate that the method can provide information about signal generated from regions outside of an intended analysis area. The method also demonstrates that commonly used methods of defining resolution produce values that can be 2 or 3 times smaller than the diameter of the area truly analyzed by a spectrometer. @FootnoteText@ @footnote 1@ This work was supported by the US Department of Energy, Office of Basic Energy Sciences, Geosciences Program. The measurements were made in the Environmental Molecular Sciences Laboratory, a DOE User facility operated for the USDOE by Battelle Memorial Institute.

Magnetic Interfaces and Nanostructures
Room 206 - Session MI-ThA

Magnetic Devices: GMR & Tunneling

Moderator: B.A. Everitt, Seagate Technology

2:00pm **MI-ThA1 The Determination of Magnetostriction for Spin-Valve Devices with 5.0 nm and 10.0 nm Permalloy Layers*, T.J. Gafron,*** Boise State University*; S.E. Russek,* National Institute of Standards and Technology*; S.L. Burkett,* Boise State University

The objective of this study is to determine the extent of magnetostriction in spin-valves. Spin-Valves were constructed on a silicon substrate using dc magnetron sputter deposition techniques with the following structure: Ta@sub 5.0@ /NiFe@sub 5.0 or 10.0@ /Co@sub 1.0@ /Cu@sub 3.0@ /C0@sub 3.0@ /Ru@sub 0.6@ /Co@sub 2.0@ /FeMn@sub 10.0@ /Ta@sub 5.0@, where the subscripts denote the layer thickness in nanometers. The films were deposited with a magnetic field applied parallel to the substrate to align the pinned and free layers. Spin-valves were designed in a serpentine shape to maximize magnetostriction effects by increasing the device length. Device widths between 1 and 40 microns and lengths between 100 and 2000 squares were fabricated. Spin-valves tested exhibited a 5-7% change in magnetoresistance and an average ferromagnetic exchange coupling of 0.4 kA/m at 300°K. Devices were subjected to an external magnetic field while a mechanical stress was applied to the backside of the substrate. A four-point probe technique was used to measure device resistance as a function of applied field and mechanical stress. An increase in the anisotropy field, H@sub k@, is observed with increasing mechanical stress. This increase is observed for all devices tested but more distinct for those containing the 5.0 nm Permalloy. Using the curvature of the stressed sample and the thickness of the spin-valve and substrate, magnetostriction is calculated as a function of the applied stress. Results show that maximum magnetostriction occurs abruptly at lower stress values for the 10.0 nm Permalloy while magnetostriction for the 5.0 nm permalloy occurs gradually over a wider range of stress values. Magnetostriction is small (1.50 microns for the 20 micron by 1K square, 5.0 nm NiFe), but the effect is pronounced and impacts device performance as demonstrated by a shift in H@sub k@. Magnetostriction analysis becomes critical as both device complexity and integration levels increase.

2:20pm **MI-ThA2 Properties of GMR Multilayers Grown by RF Diode Sputtering*, W. Zou,*** University of Virginia, usa*; X.W. Zhou, R.A. Johnson,* University of Virginia*; H.N.G. Wadley,* University of Virginia, usa*; D.J. Brownell, D. Wang,* Nonvolatile Electronics, Inc.

RF diode sputtering techniques are used for the growth of giant magnetoresistive (GMR) multilayers. The performance of devices synthesized in this manner is a sensitive function of the nanoscale structure and interfacial morphology created during the condensation step of the deposition process. Systematic series of experiments have been conducted to evaluate the dependence of film morphology upon composition of conducting layer. Atomic force microscopy (AFM) shows when CuAgAu is used (instead of pure Cu) the RMS roughness is reduced but occasional hillocks are also formed. By using a newly developed embedded atom method (EAM) alloy potential, a Molecular Dynamics study has been used to investigate the layer by layer growth phenomena and to identify the origin of the relationships between the experimental observations and layer composition. The use of the copper silver gold alloy is found to promote smoother interfaces because silver acts as a surfactant. Surface Auger results reveal the hillocks to be rich in silver a consequence of surface segregation into islands. Novel deposition strategies for morphology control have been proposed.

2:40pm **MI-ThA3 GMR Sensing Elements for the Detection of Magnetic Microbeads in Biosensor Array*, M. Miller,*** Naval Research Laboratory **INVITED**

Giant magnetoresistance (GMR) magnetoelectronics has been an area of growing technological and commercial interest. GMR hard disk read heads have enabled a order-of-magnitude increase in storage density. Nonvolatile random access memory (NVRAM) utilizing GMR technology is an area of intense research and prototype devices are being introduced. Still other devices include magnetic field sensors as well as rotation and displacement sensors. A unique application for GMR devices is in the detection of magnetic microbeads commonly used in biological research for cell and biomolecule separation. We are developing a biosensor, the Bead ARray Counter (BARC),@footnote 1@ that uses these microbeads as labels to detect DNA hybridization at specific areas over an array of GMR sensors micro-fabricated on a chip. Eventually, the BARC chip is envisioned to be akin to GMR NVRAM, with millions of sub-micron GMR elements enabling simultaneous detection of thousands of DNA sequences with high sensitivity and dynamic range. We will discuss the special magnetotransport, micromagnetics, and microfabrication issues required for the development of high-density GMR-based biosensor arrays. This work was done in collaboration with P.E. Sheehan, R. L. Edelstein, C. R. Tamanaha, L. Zhong, S. Bonnak, R. J. Colton, L. J. Whitman, and G.A. Prinz. @FootnoteText@@footnote1@Edelstein et al., Biosensors & Bioelectronics 14, 805 (2000).

3:20pm **MI-ThA5 Preparation of Magnetic Tunnel Junctions by Ionized Atom Beams*, S.O. Demokritov*,** *B.F.P. Roos, B. Hillebrands,* University Kaiserslautern, Germany

A new oxidation technique for the preparation of thin insulating barriers for magnetic tunnel junctions combined with in-situ resistivity and optical reflectivity measurements is studied. A highly dissociated low energy (30 eV-80 eV) ionized oxygen atom beam from a novel type of an electron cyclotron wave resonance controlled plasma reactor is used to oxidize metallic Al layers and to form an insulating barrier for tunnel junctions. The oxidation process is found to be self limiting. The oxidation depth variate from 1.5 to 2 nm in agreement with performed Monte Carlo simulations.

3:40pm **MI-ThA6 Nonlinear Magneto-Optical Investigations of Magnetic Interfaces*, Th. Rasing,*** University of Nijmegen, The Netherlands **INVITED**

Magnetization induced second harmonic generation (MSHG) is a new nonlinear magneto-optical technique that combines interface sensitivity with huge magneto-optical effects. These effects are due to the simultaneous breaking of inversion symmetry (at interfaces) and time-reversal symmetry (by the magnetization). Because most magnetically ordered materials are centrosymmetric in their bulk form, MSHG is a particularly interesting probe to study the magnetization structure of the interfaces in magnetic multilayer systems. Using MSHG, we have found e.g. that the spin orientation at the interface of CoNi/Pt multilayers can be different from the bulk due to specific preparation conditions. Due to both very high magneto-optical contrast and interface sensitivity, fine details of magnetization reversal become visible with MSHG imaging that are not detectable by usual magneto-optics. MSHG also appears to be highly sensitive for the step induced anisotropy in magnetic thin films grown on vicinal surfaces. In addition, effects of interface annealing and oxidation can be observed in situ, which is of great importance for sensor multilayer structures. By using phase sensitive spectroscopic MSHG experiments, the spin-dependent interface density of states can be probed, as was recently demonstrated in a study on a Ni(110) surface. This is of great importance for the understanding of e.g. the spin dependent tunnel current in magnetic tunnel devices. Finally, the use of fs laser excitation allows the probing of ultra fast magnetization dynamics, using pump-probe techniques. Recent results of this will be discussed. Part of this work was supported by FOM, the TMR Network NOMOKE and INTAS 97-0705 (ERBFMRXCT960015) and INTAS 97-0705.

4:20pm **MI-ThA8 "Acoustical" and "Optical" Spin Modes of a Fe/Cr/Fe/Cr/Fe Multilayer with Ferro- and Anti-ferromagnetic Couplings***, **F. Nizzoli**, L. Giovannini, P. Vavassori, R. Zivieri,* University of Ferrara and INFM, Italy

A study of the in-phase ("acoustical") and of the out-of phase ("optical") spin modes in layered ferromagnetic structures with both ferromagnetic and antiferromagnetic coupling is presented, in particular for the system Fe(20Å)/Cr(20Å)/Fe(20Å)/Cr(9Å)/Fe(100Å), for which experimental Brillouin scattering data are available@footnote 1@ In our model we take magnetocrystalline, uniaxial and shape anisotropies, Zeeman interaction, bilinear and biquadratic exchange interlayer couplings into account. The magnetization equilibrium configuration is calculated as a function of the external field using the steepest descent technique. A calculation of the dynamic magnetization assumed constant in each film gives an explanation of the behavior of the two kinds of modes at different magnetic fields applied along the easy axis. The "acoustical" mode is the lowest frequency one at low applied fields, but frequency exchanges with the "optical" modes occur at higher fields. It is found that the competition between the Zeeman and the biquadratic exchange terms is responsible for the appearance of a soft mode at a critical field marking a second-order phase transition.

4:40pm **MI-ThA9 Analysis of Tunneling Magnetoresistance Structures by Low Energy Electron Nanoscale Luminescence Spectroscopy***, **S.H. Goss**,* The Ohio State University*; S.S.P. Parkin,* IBM Almaden Research Center*; L.J. Brillson,* The Ohio State University

The performance of state-of-the-art tunneling magnetoresistive (TMR) heads depends sensitively on the thickness of insulating layers less than a few nanometers thick which separate two magnetic films. We have used low energy electron nanoscale luminescence (LEEN) spectroscopy to observe optical emission from TMR test structures with buried insulating oxides less than a few nm thick. TMR structures grown by DC magnetron sputtering consisted of a 0.8 - 3 nm Al oxide layer on a 2.4 nm CoFe alloy (84:16) sandwiched between a multilayer metal-on-Si substrate and a 4.4 nm CoFe plus Pt overlayer. LEEN excitation energies ranging from 0.5-3 keV enabled us to distinguish between emissions from the buried oxide layers vs. the free surface. We used different compositions, thicknesses, and oxidation exposures to separate Al oxide from transition metal oxide emissions, as well as from the ambient-exposed Pt surface. A broad peak centered at 2.7 eV increased with increasing oxygen plasma exposure at constant Al thickness. It also increased with increasing Al thickness and commensurate oxygen exposure. Emission from oxidized CoFe without Al consists of a featureless emission extending from 1.5 - 3.7eV. Common to all these spectra is emission at 1.8 eV, which energy-dependent LEEN demonstrates is due to the ambient-exposed Pt. Finally, spectral changes of the buried, oxidized Al/CoFe sandwich layers as a function of thickness and oxygen exposure reveal the regime separating oxidation of the Al layer alone from over-oxidation that extends into the CoFe base layer. These results suggest that optical emission from nanometer - thick tunnel layers within TMR structures can be used to assess the extent of oxidation as well as to optimize deposition and process conditions.

5:00pm **MI-ThA10 Magneto-optical and Optical Spectroscopies of Fe/Si Multilayered Films***, **Y.P. Lee**, T.-U. Nahm, C.O. Kim,* Hanyang University, Korea*; Y.V. Kudryavtsev,* Institute of Metal Physics, Ukraine*; K.W. Kim,* Sunmoon University, Korea*; J.Y. Rhee,* Hoseo University, Korea*; J. Dubowik,* Institute of Molecular Physics, Poland

Fe/Si multilayered films (MLF) exhibiting a strong antiferromagnetic (AF) coupling were studied by optical and magneto-optical spectroscopies. The first set of Fe/Si MLF with a fixed Fe sublayer thickness of 3.0 nm and a variable thickness of Si sublayers (1.0 - 2.2 nm) was prepared by rf-sputtering onto glass substrates at room temperature with the number of repetition of 50. To replicate the spacer silicide layers in the MLF, the second set of Fe/Si MLF with very thin Fe and Si sublayers (0.3 - 0.8 nm and 0.4 - 0.8 nm, respectively) was also deposited. The results were compared with the computer-simulated spectra based on various structural models of the MLF. Neither semiconducting FeSi@sub 2@ nor @epsilon@-FeSi turned out to be considered as the spacer layer for a strong AF coupling. The optical properties of the spacer extracted from the effective optical response of the MLF strongly support its metallic nature. A reasonable agreement between experimental and simulated equatorial-Kerr-effect spectra was obtained with the fitted optical parameters of the spacer for the FeSi or Fe@sub 5@Si@sub 3@ stoichiometry. A comparison of the extracted optical properties for the spacer with the calculated ones based on the first principles showed that a B2-phase metallic FeSi compound is spontaneously formed at the interfaces of MLF during deposition. For the Fe/Si system with ultrathin Fe and Si sublayers, our optical data reveal that the overall structure of MLF is close to an amorphous and semiconducting @epsilon@-FeSi.

MEMS
Room 309 - Session MM-ThA
Material Science of MEMS

Moderator: C.C. Wong, Sandia National Laboratories

2:00pm **MM-ThA1 Stress Measurement in MEMS Devices***, **L.A. Starman**,* Air Force Institute of Technology*; J.D. Busbee,* Air Force Research Laboratory Materials Directorate*; J. Reber,* Wright State University*; J.F. Maguire, W.D. Cowan,* Air Force Research Laboratory Materials Directorate

Due to the unique structure and small scale of Micro-Electro-Mechanical Systems (MEMS), residual stresses during the deposition processes can have a profound affect on the functionality of the MEMS structures. Typically, the material properties of thin films used in surface micromachining are not controlled during deposition. Currently, few techniques are available to measure the residual stress in MEMS devices, with each having a limited degree of validity. In this paper, Raman imaging spectroscopy is utilized to examine the residual and induced stress in silicon MEMS test structures. As MEMS structures become more complicated, images generated from Raman spectroscopy can provide valuable information on stress fields in the structure. Since the Raman methodology is directly sensitive to stress in the deposited material, the potential exists for this technology to be used both as an in situ quality control device and for the control of gradients in the batch processing. Successful implementation of this technique allows the validation of MEMS designs. We report here the mapping of the complete stress field across a micromirror flexure. Vertical displacement measurements obtained using an interferometric microscope allow the applied stress in the device flexures to be calculated as a conformation of the stress image.

2:20pm **MM-ThA2 Issues in MEMS Reliability and Characterization***, **S. Brown**,* Exponent, Inc. **INVITED**

This presentation addresses MEMS failure modes that are either unexpected or judged insignificant on a macroscale. Although MEMS devices can fail from typical "macro" effects such as overload, fatigue, or corrosion, in many instances these phenomena are accentuated once one addresses micron sized devices. Examples cited include stress corrosion of silicon, creep of membrane and thin film structures, electrostatic accumulation, shock resistance, and strength reduction due to processing effects. Possible countermeasures are included with each example, and suggestions are provided for additional investigation on MEMS reliability.

3:00pm **MM-ThA4 MOCVD PZT as a Pathway to Integrated Piezoelectric MEMS***, **I.-S. Chen**, J.F. Roeder,* ATMI*; D.-J. Kim, J.-P. Maria, A.I. Kingon,* North Carolina State University

Development of reliable actuation methods is one of many challenges in thin film MEMS devices. Piezoelectric actuation using bulk ceramic materials is well known, but widespread use in MEMS requires suitable deposition and integration methods that are compatible with large-scale manufacturing. One primary factor limiting the development of piezoelectric MEMS has been the lack of a suitable thin film piezoelectric material. PZT and its derivatives have excellent piezoelectric properties and therefore are a logical choice for MEMS applications. Metalorganic Chemical Vapor Deposition (MOCVD) offers a unique combination of precise composition control, uniformity over large areas, and relatively low process temperatures that are compatible with integrated Si processing. We have developed MOCVD processes to prepare PZT films on advanced electrodes with longitudinal piezoelectric coefficients (d@sub 33@) up to 50pm/V. Robust electrode stacks were developed to suppress diffusion of reactive / mobile species into the silicon substrate during PZT deposition. The electrode stacks are fully compatible with substrates typically used in bulk micromachining, namely silicon wafers coated with either silicon nitride or boron-doped epitaxial silicon as an etch stop. For temperature-critical surface-micromachined structures, process temperatures as low as 450 °C have been successfully demonstrated.

3:20pm **MM-ThA5 Deposition of Highly Oriented LiCoO@sub 2@ Thin Films for Use as Cathodes in Thin Film Batteries***, **J.A. Ruffner**, T.J. Boyle, D. Ingersoll, K.P. Peters, M.A. Rodriguez, J. Liang,* Sandia National Laboratories

Presently micro-and meso-machines (MEMS) are powered by sources that are large in comparison to the actual MEMS devices. Development of small-scale power sources is critical if these devices are to reach their full usefulness. A prototype all-ceramic thin film battery that consists of a LiCoO@sub 2@ cathode, surface modified silica film composite electrolyte, and SnO@sub 2@ anode is presently under development at Sandia National Labs. Deposition of well-oriented, crystalline LiCoO@sub 2@ thin film cathodes is a critical step to achieve the highest capacities possible for these batteries. LiCoO@sub 2@ thin films deposited at ambient temperature using rf sputtering are generally amorphous in their as-deposited state. Post deposition annealing at temperatures > 300 °C results in melting and subsequent crystallization.@footnote 1@ However, it may be possible to promote crystallinity in the desired orientation [(101), (100) or (104) planes parallel to the substrate] by using a substrate or appropriate seed layer which is epitaxially matched to the desired LiCoO@sub 2@ orientation. Single-crystal metal substrates, such as Au (110), Re (100), or Ti (100), have lattices that are well-matched to LiCoO@sub 2@ lattices. However, these substrates are expensive and, in the case of Ti, readily oxidized. Instead, we deposited thin films of these metals as seed layers on more readily available single-crystal dielectric substrates (i.e. quartz) in order to test their effectiveness in promoting crystallization of subsequently deposited LiCoO@sub 2@ thin films in the desired orientation. We report on the orientation and properties of LiCoO@sub 2@ thin films deposited using rf sputter deposition versus solution chemistry. 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. @FootnoteText@ @footnote 1@ P. da Fonseca et al., J. Power Sources (1999), 81-82, 575-580.

3:40pm **MM-ThA6 Microstructure and Mechanical Properties of Polysilicon and Poly-SiC Films for MEMS***, **H. Kahn**, A.H. Heuer,* Case Western Reserve University **INVITED**

Polysilicon films deposited via LPCVD are the current mainstay structural material for MEMS. It is well known that the microstructures and residual stresses of these films are influenced by deposition temperature. We have developed a novel processing approach (the MultiPoly process) which exploits this concept by using polysilicon multilayers in order to create flat structures, as well as structures with controlled curvatures. The effect of microstructure on mechanical properties is less well known. We have also developed a surface-micromachined electrostatic microactuator capable of generating 0.7 mN of force. The microactuator can be integrated with on-chip fracture mechanics specimens, and these devices have been used for studying strength, toughness, and fatigue resistance of polysilicon. Similar studies have also been done on poly-SiC films.

4:20pm **MM-ThA8 Comparison of In-situ Boron-doped and In-situ Phosphorus-doped Polysilicon Films for Microelectromechanical Systems***, **J.J. McMahon**, J.M. Melzak, C. Zorman, J. Chung, M. Mehregany,* Case Western Reserve University

In order to produce thick polysilicon films for MEMS applications, a single step, high deposition rate, APCVD process was developed and used to deposit in situ boron-doped, undoped, and in situ phosphorus-doped polysilicon films at susceptor temperatures ranging from 625C to 850C. For doped and undoped films alike, the deposition rate increases with increasing susceptor temperature, with boron-doped films exhibiting the highest deposition rate at each temperature setting. The highest deposition rates occurred at 850C, with boron-doped films being deposited at a rate of 733A/min, undoped films at a rate of 716A/min, and phosphorus-doped films at a rate of 622 A/min. Spreading resistance and SIMS measurements performed on the boron-doped samples indicate that the boron concentrations are generally constant throughout the thickness of the films, with the highest boron concentrations found in films deposited at 625C. Wafer curvature measurements on boron-doped films indicate that the films are in compression over the entire temperature range, with the magnitude of the stress decreasing with increasing temperature. In contrast, the undoped films are in tension at lower temperatures, but become compressive as the deposition temperature is increased. TEM analysis shows that film microstructure strongly depends on the deposition temperature, with equiaxed grains forming at low substrate temperatures and columnar grains forming at higher temperatures. Surface micromachined cantilevers, strain gauges, and lateral resonators were successfully fabricated from 5.0 micron-thick doped films grown at 850C. The extended paper will detail the process used to deposit the doped and undoped films, present a summary of the characterization study, and highlight the performance of micromachined structures and devices.

4:40pm **MM-ThA9 Investigation of the Friction and Adhesion Properties of BPT and BPTC Self-assembled Monolayers by AFM***, **H. Liu**, B. Bhushan,* The Ohio State University*; W. Eck, V. Stadler,* University of Heidelberg, Germany

Self-assembled monolayers (SAMs) are considered to be good candidate lubricants for microelectromechanical systems (MEMS). It is important to understanding the relationship between the structure and tribological performance for molecular tailoring to achieve efficient lubrication. For this purpose, biphenyl-4-thiol (BPT), and cross-linked biphenyl thiol (BPTC) were prepared on a gold sublayer. The cross-linking of BPT was carried out by low energy electron irradiation. Structure characterization shows that cross-links were formed between neighboring phenyl groups. The topography, adhesion, and friction properties of Si, Au, BPT and BPTC were studied by atomic force microscopy (AFM) with silicon nitride tip. It was found that both BPT and BPTC exhibited lower adhesion and friction than Si. But the coefficient of friction of BPTC are higher than BPT. The larger coefficient of friction of BPTC is believed to be caused by its rigid cross-linked structure. The study also found that the topography of different films have different contribution to the frictions of films. For Au and BPTC, friction is affected by surface slope, but for BPT the higher surface areas have low friction. A relationship between wear resistance of the low friction phase of BPT and its size was found.

5:00pm **MM-ThA10 Viewing a Moving Surface Contact: An STM-QCM Study of Vapor Deposited Films on Metal Surfaces***, **B. Borovsky**, M. Abdelmaksoud, J. Krim,* North Carolina State University

With the emergence of MEMS technology and the problems of high friction and mechanical failure encountered in the operation of such devices, new experimental techniques are needed which are able to probe nanometer scale contacts under sliding conditions relevant to MEMS. By combining a Scanning Tunneling Microscope (STM) with a Quartz Crystal Microbalance (QCM), we have constructed a nanotribological test set-up in which a single asperity contact is subject to contact pressures and sliding speeds relevant to both MEMS and macroscopic devices. We have applied STM-QCM to the study of vapor phase lubricants, which may prove to be an effective, and perhaps exclusive, means of lubricating MEMS devices. The STM allows direct imaging of the surface contact under both stationary and vibrating conditions, and is able to track changes in the conductivity and mobility of molecularly thin lubricant films. Surprisingly, the amplitude and speed of the sliding contact may be directly measured using STM images of the vibrating QCM surface. We show that the QCM achieves sliding speeds over 1 m/s and senses changes in sliding friction as a function of normal load upon application of a lubricant film to a bare metal surface. Together, our nanometer scale STM-QCM results are highly suggestive of the known macroscopic lubricant properties of the applied films. By performing rubbing-and-imaging experiments with this combined apparatus, dramatic changes in the properties of the contact are observed which are highly localized to the region of rubbing. Such investigations provide evidence of possible tribochemical effects, the observation of which is associated with the realistic sliding conditions attained with the STM-QCM. Research supported by the NSF and the AFOSR.

Manufacturing Science and Technology
Room 304 - Session MS-ThA

Advanced Modeling for IC Manufacturing

Moderator: E.G. Seebauer, University of Illinois, Urbana-Champaign

2:00pm **MS-ThA1 Challenges in Modeling & Simulation of Semiconductor Equipment & Processes*, A.K. Das,*** Applied Materials Inc. **INVITED**

Modeling & simulation of semiconductor manufacturing equipment & processes is an inherently multi-disciplinary effort drawing from such diverse fields as plasma physics/chemistry and heat and mass transfer. Over the past few years, significant strides have been made to address and incorporate several of these phenomena, and enable optimization of chamber geometry and processes through modeling. However, many of these physical phenomena occuring in processing equipment are not even well understood or characterized. Obtaining self-consistent models that combine the influences of different phenomena or different aspects of processes is perhaps the major hurdle between where we are now and taking comprehensive reactor models (or the Virtual Reactor) mainstream. There are several issues that must be resolved before comprehensive reactor models may become commonplace. The computer model must be able to handle stiff chemistry-equations and the resulting numerical convergence problems. In plasma modeling, the sheath must be resolved properly to predict the ion flux and energy at the wafer surface. The extension of fluid models into the transition regime must be incorporated in the commercial codes. Finally ways must be explored to combine the reactor level model with the device/feature level. Currently setting up a model may be very time-consuming due to the lack of smart grid generation tools. The proliferation of modeling to the common engineer cannot happen without streamlining and minimizing the grid-generation effort. Lastly, there is a lack of fundamental or often tool-specific data necessary to accurately simulate these processes. Most of the reaction mechanisms/pathways of relevance to real processes are not well understood. A long-term sustained research effort is required from chip-makers, equipment companies, academia, national laboratories and commercial software developers to overcome these shortcomings.

2:40pm **MS-ThA3 Modeling of Oxide CMP and Polish Pad Conditioning*, L. Jiang,*** Intel Corp., US*; H. Simka, S.S. Shankar, J. Su, K. Kumar, V. Murali,* Intel Corp.

A model for the mechanical and chemical aspects of oxide CMP is presented. We combined both contact mechanics and slurry flow in a physical model (Jiang & Shankar 1999) and compared the simulation results to recent studies on oxide CMP. Pad asperity deformation and slurry flow between asperities are modeled simultaneously. Dissolution and polish rates of oxide are modeled based on silica hydrolysis kinetics and calibrated with experimental data. Mechanisms of pad glazing and conditioning effect on polish rate are also discussed with a review of literature data. Pad glazing is a result of mechanical (cyclic polish stress) and chemical actions (oxidation of surface during polish). Pad degradation effects on polish rate over the wafer scale are predicted by combining pad fatigue model with mechanics/flow simulations. Relative motions between pad, wafer, and individual conditioner heads are simulated to predict pad conditioning effectiveness and pad age.

3:00pm **MS-ThA4 Mechanical Properties of a Cu-Ta Interface by Molecular Dynamics***, P. Heino,* ***E. Ristolainen,*** Tampere University of Technology, Finland

During last few years, the electrical and mechanical properties of copper have received a lot of interest in the electronics community, mainly because of its low electrical resistance. Last year at AVS1999@footnote 1@ we discussed mechanical properties of nanoscale copper connection and concentrated on pure copper. In this work we study the microstructure and strength of the copper interface. To prevent diffusion of copper into silicon, a barrier is needed. Furthermore, the barrier-copper system should be immiscible. It seems that tantalum is used most often as a barrier metal, and it has the needed properties. Here we study the copper-tantalum interface by means of molecular dynamics method and embedded atom potential. In the model the cross term potential has been optimized to reproduce the experimental (small and positive) heat of alloy formation. The interface is formed by depositing Cu on different single crystal Ta surfaces. The microstructure and properties under shear of the resulting interface are analyzed. @FootnoteText@@footnote 1@P. Heino, P. Holloway and E. Ristolainen: Strength of Nanoscale Copper Under Shear, Accepted for publication, J. Vac. Sci. Tech. A (2000).

3:20pm **MS-ThA5 Integrating Process Models, Equipment Logistics, and Factory Flow for Manufacturing Systems Optimization*, L. Henn-Lecordier,*** University of Maryland, US*; M.-Q. Nguyen, B. Conaghan, P. Mellacheruvu, J.W. Herrmann, G.W. Rubloff,* University of Maryland

Technology change, yield learning, and market shifts all produce notable factory dynamics, yet anticipating the operational consequences of process changes and optimizing the overall system remains largely an ad hoc procedure. We have developed a heterogeneous simulation environment (HSE) which integrates process and operational dynamics from the unit process to full factory flow. Process models are incorporated as response surfaces which determine cycle times in corresponding equipment modules. In turn, the operational behavior of multiple modules on cluster tools is investigated through discrete event simulation for specific cluster tool architecture, module population, and scheduling algorithms. Finally, process and cluster tool models are incorporated into factory-level discrete event simulations (Factory Explorer). Management of process, equipment, and factory parameters, as well as model execution, is carried out through a simulation supervisor and its graphical user interface. These integrated models enable tradeoff analysis involving specific process parameters, cluster tool configuration and logistics, and factory flow as a function of tool populations. We have studied the specific example of a W plug process sequence, involving clean, PVD TiN liner deposition, and W CVD fill. Results indicate notable cycle time advantage for individualized cluster tool sequencing optimized for the chosen process parameters, as compared to using routine dispatching rules. The HSE also reveals the factory level operations consequences of re-entrant flow, where the dimensions of different interconnect levels produce different throughputs for different levels. Thus, the HSE presents a potentially valuable tool for rapid optimization in the presence of factory dynamics, usable by operations, equipment, and process engineers.

3:40pm **MS-ThA6 Plasma Reactor Simulation to Improve Film Deposition Uniformity*, K. Bera,*** *K. Liu,* Applied Materials, Inc.

A capacitively coupled plasma discharge has been simulated for an industrial reactor to investigate the uniformity of the film deposition profile on the wafer. The gap width between the powered cathode and the ceramic wafer pedestal is very small compared to the radius of the cathode. Non-uniform grid is used to resolve the sheath in the plasma for this reactor configuration. Silane is fed as a feed gas from the showerhead into the chamber at low pressure. The spatial distributions of electron, ion and radical densities, electron temperature and ion energy are obtained using Plasma Reactor Simulator (PRSim) code. The spatial distributions of radical flux and ion energy on the wafer are useful for the prediction of thin-film deposition rate. The effect of the distance of wall dielectric from the wafer edge on the surface process is also investigated. A mixture of silane and nitrous oxide is fed in the chamber to investigate the effect of silane dilution on the process. The present study is used to identify the reactor design condition to achieve uniform film deposition rate on the wafer.

4:00pm **MS-ThA7 First Principles Modeling of Gas-Surface Interactions in Low Pressure CVD Processes*, H. Simka,*** *S.S. Shankar,* Intel Corp.*; J.-R. Hill, S. Mumby,* Molecular Simulations, Inc.

Understanding and optimization of low-pressure CVD systems typically necessitate knowledge of interactions between gas-phase species and surface at the molecular level. A physically-based approach to model these interactions is presented. The approach is based on ab-initio quantum chemistry investigations of molecular and surface properties, as well as binding between reactive gas-phase precursors with atoms on the growth surface. Application of the method to low-pressure CVD of silicon nitride using dichlorosilane (DCS) and ammonia will be illustrated. Energetics of the gas-surface interactions are calculated using density-functional theory (DFT), with the surface represented by H-terminated clusters involving the active centers. Energy values obtained using DFT methods for this system are typically more accurate compared to those obtained using semi-empirical methods. For example, the activation barrier for gas-phase decomposition of DCS to SiHCl and HCl calculated using the PM3 semi-empirical method is 45 kcal/mole, which is significantly lower than values obtained using DFT and more accurate ab-initio methods such as G2 (65 to 68 kcal/mole). Other comparisons illustrating further limitations of the semiempirical method for modeling of gas-surface interactions will be presented. Reactivity of several surface sites in the cluster model is investigated. Adsorption energies of several gas-phase species are calculated; accuracy of the several DFT methods used is evaluated and will be discussed.

4:20pm **MS-ThA8 Etching of Silicon in HBr Plasmas for High Aspect Ratio Features*, H.H. Hwang,*** ELORET Corp.*; G.S. Mathad, R. Ranade,* Infineon Technologies, Inc.*; M. Meyyappan,* NASA Ames Research Center

Acquiring straight wall etching is a continuing goal in the semiconductor processing industry. Achieving a vertical wall with no bowing becomes extremely critical as dimensions decrease to less than 0.1 µm. Undercutting must be minimized in order to obtain closely spaced features of this size. Etching typically requires aspect ratios on the order of 20:1 (depth:width) and often higher than 50:1. At these small feature sizes and large aspect ratios, neutral shadowing becomes increasingly more important. Fewer neutral radicals which can passivate the substrate surface can enter the trench opening, which leads to a decreased etch rate and can limit the maximum obtainable aspect ratio (AR). In pure chlorine, for example, it is difficult to achieve ARs of more than 5:1. To date, however, most modeling efforts have not focused on the specific problems encountered in high aspect ratio etching. We will present results for etching silicon in HBr plasmas using a previously developed feature profile evolution simulation using a level set method (SPELS). We will compare calculated average etch rates, total etched depth, and RIE lag effects (etch rate dependence on feature size) in high aspect ratio trenches to experimental measurements. The measurements were made in a parallel plate, capacitively-coupled, magnetically enhanced reactor. We will also present comparisons in etch rates for different feature sizes (0.2 µm, 0.175 µm, and 0.15 µm). Comparisons of simulated etched profiles and experimentally obtained SEMS will also be presented.

4:40pm **MS-ThA9 Contamination Removal from Wafer with Deep Trenches*, H. Lin,*** *A.A. Busnaina, I.I. Suni,* NSF and CAMP (New York Center for Advanced Materials Processing, at Clarkson University)

The International Technology Roadmap for Semiconductors shows the requirement for high aspect ratio (depth/width) trenches in DRAM trench capacitor technology. Cleaning high aspect ratio deep trenches is challenging because of the need to rinse or remove contaminants from the bottom of trench. In this work, based on the experimental and numerical study of blanket wafer cleaning, contamination removal from wafer with topography is studied using physical modeling. The rinsing flow and contaminant transport in the geometry are modeled by solving the governing momentum and mass conservation equations with associated boundary conditions. The rinsing of patterned wafer is accomplished using an oscillating flow past a series of high ratio rectangular trenches. The modeling results of flow past a series of trenches show a good agreement with the experimental results of Perkins. Oscillating flow rinse is found to be more efficient than steady flow rinse using the same average rinsing velocity. The effects of the aspect ratio, trenches size, and oscillating flow frequency on cleaning efficiency are presented.

5:00pm **MS-ThA10 In Situ Metrology for Cu Electroplating*, G. Barna,*** Texas Instruments, US

This presentation will describe the use of the RTA (Technic, Inc.) system for control of a Cu plating bath in a SC productization environment. This tool is a robust, in-situ sensor that analyzes all the components of the bath by a variety of electroanalytical techniques. It consists of a probe that stays continually immersed in the main bath module of the plater, with the appropriate electronics and PC controller located within 25 ft. of the probe. A complex factory calibration scheme provides accurate measurements. The internally generated reference electrode and the rigorous electrochemical cleaning procedures provide long-term repeatability and reliability. Measurements of all 5 components are performed in ~ 15 minutes, making repeated measurements easy. Long-term sensor stability has been demonstrated. After a year of continuous use, this sensor has required no recalibration and virtually no maintenance. Bath control is greatly facilitated by the accuracy, repeatability and reliability of this sensor. Its CoO is minimal, there is no need for any standards or test solutions and its cleanroom footprint is no larger than a PC. Further development of this system, aimed to provide information over and above simple bath control, will also be described.

Processing at the Nanoscale/NANO 6
Room 302 - Session NS+NANO6+MC-ThA

Near-field Optics and Photonics

Moderator: Y. Kuk, Seoul National University, Korea

2:00pm **NS+NANO6+MC-ThA1 Optical Sieves - How to Get the Light through Subwavelength Holes*, T.W. Ebbesen,*** Louis Pasteur University, France **INVITED**

Metallic films perforated with sub-wavelength holes (~150 nm) can transmit the light with an efficiency thousand times larger than what theory predicts for single holes. The efficency can even be larger than the fractional area of the holes, which means that even the light falling beside the holes emerges on the other side of the sample. This extraordinary transmission is due to the coupling of the incident light with the surface plasmons of the film. The transmission spectrum contains peaks attributed to surface-plasmon modes that depend on both the symmetry and the 2D lattice parameter of the surface corrugation. We have shown that this phenomenon can also be used to tune and enhance the transmission of single subwavelength aperture. These results have broad fundamental and practical implications and show that, with modern fabrication techniques, surface plasmons can be engineered and controlled to yield unique optical properties.

2:40pm **NS+NANO6+MC-ThA3 Near-field Optical Measurements of Two Types of the Super-resolution Near-field Structures*, D.P. Tsai,*** National Taiwan University, Taiwan*; W.C. Lin,* National Taiwan University

Two different types of super-resolution structures for the near-field optical storage were studied. Direct experimental observation of the near-field optical properties in the super resolution near-field structures of glass/SiN(170nm)/Sb(15nm)/SiN(20nm) and glass/ZnS-SiO2(20nm)/AgOx(15nm)/ZnS-SiO2(20nm) have been achieved by using a tapping-mode tuning-fork near-field scanning optical microscope. Both propagating and evanescent field intensities were found at the focused spots of the surfaces of the super resolution structures. The evanescent intensity may result from the localized surface plasmons excited at the antimony or silver oxide. Images of the near-field intensity gradients at different excited laser powers demonstrated that the area had the static evanescent intensity could be stably controlled. Direct observation of the focused spot sizes of the static evanescent field intensity and their changes controlled by the excited laser power have demonstrated the working mechanism of both two types of super-resolution structures.

3:00pm **NS+NANO6+MC-ThA4 Near Field Surface Photovoltage Microscopy**, *R. Shikler, S. Saraf,* ***Y. Rosenwaks,*** Tel-Aviv University, Israel

Surface photovoltage (SPV) is a well-established technique for the characterization of semiconductors, which is based on analyzing illumination-induced changes in the semiconductor surface potential. The SPV and other related techniques like surface photovoltage spectroscopy (SPS), has been successfully used to study metal-semiconductor interfaces, surface states, bulk defects, and minority carrier lifetime and diffusion length. To date, all the SPV related technique have a common significant drawback: they do not have high spatial resolution. With the developments of scanning probe microscopy techniques in recent years, the way is paved to conduct SPV measurements with nanometer lateral resolution. In this talk we describe a novel technique called near-field photovoltage (NFPV) which measures the SPV using near-field optical force sensor. The key feature of the technique is that the excited semiconductor sample is in the optical near- field region of a pulled optical fiber that measures the contact potential difference (CPD) between the fiber and the sample using the Kelvin probe force microscopy (KPFM) method. In such a case the illumination spot size is determined by the diameter of the aperture at the end of the tip and is not limited by diffraction. In addition, the light propagation is evanescent i.e. the intensity of the light falls off exponentially with increase distance from the tip edge (perpendicular to the crystal surface). This in combination with the high spatial resolution of the KPFM makes it possible to obtain depth-sensitive two-dimensional photovoltage images in semiconductors, and other materials. The method is demonstrated by photovoltage measurements conducted on buried p-n junctions of III-V compound semiconductors. . When the sample was excited under far-field conditions, a decrease in the PV of the whole structure was observed due to a larger photovoltaic effect (band flattening) in the p-n junction. This is due to the fact that under super-bandgap illumination the band bending of the p-n junction decreases and causes a decrease of the structure work function. On the other hand, when the sample was excited and measured with the near-field optical force sensor, an increase in the PV was observed due to band flattening only in the surface space charge region. Our results demonstrate the large surface sensitivity of the NFPV technique, and opens the way for a variety of ultra-surface sensitive SPV measurements and applications.

3:20pm **NS+NANO6+MC-ThA5 Dual-Wavelength Scanning Near-Field Optical Microscopy**, ***P.R. LeBlanc**, M. Gu, P. Grutter, D.G. Gray,* McGill University, Canada

We have developed a Dual-Wavelength Scanning Near-Field Optical Microscope to shed light onto the scanning process and investigate biological samples in air. We couple 442 and 325 nanometer light into a tapered optical fiber glued to a quartz tuning fork which serves as our `shear-force' sensor. Light transmitted through the sample is detected in a confocal arrangement by two photomultipliers. We have achieved topographical and optical resolutions of 10 and 30 nanometers, respectively. The dual-wavelength nature of our microscope permits the discrimination of topographical and optical cross-talk. It also allows the distinction of far-field artifacts from near-field features. Our primary biological application of the microscopy focuses on the investigation of the lignin distribution in wood fibers. Lignin, a cross-linked phenolic polymer, is of paramount importance in the pulp and paper-making processes. Our instrument permits the discrimination between chemical species density and topographical variations of the sample. The ratio of the two wavelength channels provides a simple and accurate parameter to determine the local concentration of lignin. These studies agree with atomic force microscopy images of wood cells and ultraviolet studies of wood cell walls.

3:40pm **NS+NANO6+MC-ThA6 Novel Scanning Near-field Optical Spectroscopy/Atomic Force Microscope Probes with High Polarisation Single/Double Slit and Cross Aperture Tips**, ***H.P. Zhou**,* University of Glasgow, UK, United Kingdom*; G. Mills, L. Donaldson, J.M.R. Weaver,* University of Glasgow, UK

We have developed novel scanning near-field optical microscopy/atomic force microscope (SNOM/AFM) probes. These probes have high polarisation single/double slit and cross apertures situated at the hollow tip apex of a silicon nitride cantilever. Direct-write electron-beam lithography (EBL) and silicon micromachining are used in a reliable batch process. The apertures are defined by lithographic means, therefore, the size, shape and orientation of apertures are well controlled and reproducible. The integration of a conventional force microscope cantilever with the aperture allows reliable control of the aperture-sample distance. The cross aperture probe has two very narrow orthogonal slits which have a width of much smaller than a wavelength, and a length on the order of a wavelength. We have designed and constructed a SNOM system based on the cross aperture probes. A parallel-polarised (p polarised) beam passes through the vertical slit and illuminates a sample hold in the near field of the aperture. The reflected light from the sample with the incident polarisation is received by the same slit, while the perpendicular-polarised (s polarised) fluorescent component is received by the horizontal slit. Using this system, we have obtained near-field fluorescence imaging and have demonstrated spectrally resolved photoluminescence imaging with a spatial resolution of 50nm. The single and double slit apertures are vertically or horizontally oriented. The polarisation properties of the optical transmission from the slit aperture probes have been investigated as a function of the polarisation orientation. The polarisation behaviour of the slit probes is linearly polarised. The polarisation ratio ranged from 1:60 to 1:1000 for different ratios of length to width of slits.

4:00pm **NS+NANO6+MC-ThA7 Optical Properties of Strained GaInP/InP Quantum Dots Studied with STM Based Electro-luminescence**, ***M.K.-J. Johansson**, U. Hakanson, J. Johansson, M.-E. Pistol, L. Montelius, L. Samuelson,* Lund University, Sweden

The physics of nanometer scale structures has become a rapidly evolving field sparked by considerable interest from both science and technology. In the effort to assess the optical properties of individual nano-structures the use of scanning tunneling microscopy (STM) as the excitation source has received a lot of attention.@footnote 1@ Compared to more conventional techniques such as photoluminescence and cathodoluminescence the excited volume is very small and a further advantage is that the excitation energy can be greatly varied, from resonant conditions to above the impact ionization threshold. In addition STM provides very detailed information of the electronic structure and thus a manifold of data can be obtained within the same experiment. Here we will present measurements using a variable temperature UHV-STM combined with a scanning electron microscope. Furthermore, the system is equipped with an ex-situ laser source and optical detection system allowing a combined study of STM based electroluminescence, laser induced photoluminescence and cathodoluminescence to be performed without the need to change experimental conditions and set-up. In this report we investigate the optical properties of capped InP quantum dots grown by metalorganic vapor phase epitaxy on a highly doped GaInP layer, lattice matched to GaAs grown on a GaAs(001) substrate. We discuss the mechanisms of inducing luminescence and the dependence on excitation energy using the InP quantum dots as a model system. @FootnoteText@ @footnote 1@See for instance, A. Gustafsson et al. J. Appl. Phys. Rev. 88, 1715 (1998) and references therein.

4:20pm **NS+NANO6+MC-ThA8 Silicon Nanostructures via Intense Ultrafast Electronic Excitation**, ***A.V. Hamza**, M.W. Newman,* University of California, Lawrence Livermore National Laboratory*; T. Schenkel,* University of California, Lawrence Berkeley National Laboratory*; H.W.H. Lee,* University of California, Lawrence Livermore National Laboratory*; P. Thielen,* University of California, Lawrence Livermore National laboratory*; J.W. McDonald, D.H. Schneider,* University of California, Lawrence Livermore National Laboratory

Due to the indirect nature of its band gap, bulk silicon is typically a poor photon emitter upon external excitation. However, as the crystal size approaches nanometer scales, the band gap widens due to quantum confinement and may become direct allowing for more efficient photon emission. Phase transformations induced by intense, ultrafast electronic excitation from slow, highly charged ions have produced nanometer-sized structures in silicon. Beams of highly charged ions of various charge state from 20+ to 69+ and various kinetic energies from 5 to 14 keV times charge have been utilized to induce this phase transformation in clean, silicon surfaces. The new phase is characterized by ex situ photoluminescence from the irradiated area after excitation with laser wavelengths from 379 - 514 nm. Photoluminescence spectra from the exposed areas show emission centered at ~540 nm. This is consistent with emission observed from 1-2 nm silicon nanocrystals. A series of sharp lines at 565, 555, and 548 nm are present in the photoluminescence spectrum from areas exposed to Xe@super 44+@ which are characteristic of an excitonic series in nanometer-sized material.

4:40pm **NS+NANO6+MC-ThA9 Microstructural and Optical Properties of Porous SiC**, *S. Zangooie,* University of Nebraska, Lincoln*; H. Arwin,* Linkoping University, Sweden*;* ***J.A. Woollam**,* University of Nebraska, Lincoln

Electrochemical etching of crystalline SiC in hydrofluoric acid creates a high surface area material with room-temperature light-emitting properties stronger than those obtained from bulk SiC. The luminescence properties of porous SiC (PSC) open up application possibilities with, e.g., SiC-based integrated electronics. Applications of PSC demand a detailed understanding of microstructure and its relation to different fabrication parameters. In this work, ellipsometry and electron microscopy are used for characterization of 4H- and 6H-PSC. The dominant surface morphology consists of branched rosette-like structures surrounding sparsely located and circularly shaped holes with diameters of the order of 20 nm or less. The density of pores descending from the surface does not show clear dependence on the etching conditions. It is likely that pore initiation is favored at certain defect sites. Pores in PSC are found to initially propagate nearly parallel to the surface and gradually change direction and align with the c-axis. Consequently, well-defined columnar pores are formed. Thickness dependent anisotropy in pore propagation influences the etch rate, which varies nonlinearly with anodization time. Etching parameters such as hydrofluoric acid concentration and current density influence the rate of change of propagation direction. Pore sizes are found to increase with depth due to a decrease in acid concentration. A disordered phase is encountered at the interface between crystalline SiC and the pores. Spectrsocopic ellipsometry is used to study the microstructure, and we find that a simple effective medium approximation assuming mixtures of crystalline SiC and void does not result in good agreement with experimental data. To obtain good agreement with thickness and porosity, the disordered phase must be consideration. Anodization of SiC introduces remarkable changes to the optical properties due to depth-inhomogeneity and particle shape effects.

5:00pm **NS+NANO6+MC-ThA10 Development of a Photon Detection STM for Inelastic Light Emission**, ***D. Fujita**, W.-L. Deng, T. Ohgi, K. Ishige,* National Research Institute for Metals, Japan

Recently it has been demonstrated that the light emission induced by tunneling electrons can be detected with normal STM operation even with atomic resolution. The possible processes are inelastic tunneling (IET) and hot-electron thermalization (HET). Generally speaking, in the case of IET, the tunneling electrons lose a part of the energy during the tunneling events to excite the state with some radiative decay processes. In the latter case, hot electrons lose the excess energy in the bulk. However, in order to get more detailed understanding of the luminescence process, much more precise measurements of these photons are required. For this purpose, we have developed a novel LT-UHV-STM system for the detection of light emission caused by the tunneling electrons. The emitted photons can be collected by the apex of a conductive and transparent optical fiber coated with a 100nm ITO (Indium-Tin-Oxide) film. Using a cooled photon detection system, single photon counting and spectroscopy with a very low noise level can be achieved. The system has been successfully applied to noble metal surfaces (Ag(111) and Cu(100)), and a direct-gap semiconductor surface (GaAs(110)) in UHV.

Plasma Science and Technology
Room 310 - Session PS1-ThA

Plasma-Surface Interactions II

Moderator: C.B. Labelle, Bell Laboratories, Lucent Technologies

2:00pm **PS1-ThA1 Plasma Surface Modification of PET and Acrylic Coating Surfaces***, **M.K. Shi,*** Pacific Northwest National Laboratory, U.S.*; A. Tyryshkin,* Princeton University*; G.C. Dunham, M. Bowman, G.L. Graff, P.M. Martin, G.J. Exarhos,* Pacific Northwest National Laboratory

Plasma treatment has proven to be very effective in modifying polymer surface properties for enhanced surface compatibility and adhesion. The treatment is performed in vacuum and the effect can be achieved within a few seconds. These characteristics make plasma technology extremely appealing for the adhesion promotion of polymer-metal multilayer stacks that can be deposited inline and at high speed in a vacuum web-coater. The surface modification of poly(ethylene-terephthalate) (PET) and UV-cured tripropyleneglycol diacrylate films induced by remote N@sub2@ and Ar microwave (2.45 GHz) plasmas was investigated in order to better understand the plasma/surface interaction mechanisms. In-situ XPS analysis revealed that N@sub2@ and Ar plasma treatments led to removal, in entirety, of the initial oxygen-containing groups on the polymer surfaces. The removal of ester groups was much faster for the acrylic than for the PET, and the removal of ether groups was much faster than that of ester groups within the acrylic film. Electron parametric resonance (EPR) measurements indicated the presence of several types of free radicals. The concentration of these radicals was higher for N@sub2@ than for Ar plasma treatment and for the acrylic than for the PET film, which correlated well with the more pronounced surface modifications measured by XPS. Pulsed EPR measurements suggested that these radicals existed mainly in radical pairs and were distributed within 2000 Å from the top surface. The concentration of free radicals correlated well with the amount of N incorporated into the surface by N@sub2@ plasma treatment. These results strongly supported a free radical-dominated plasma/surface interaction mechanism and highlighted the important role of plasma UV emission. Water contact angle measurements indicated that the incorporated N atoms were responsible for the improved surface wettability.

2:20pm **PS1-ThA2 Exploring Chemical Mechanisms behind Hydrophilic Surface Modification of Polymeric Membranes by Low-temperature Plasma Treatment***, **M.L. Steen**[1], E.R. Fisher,* Colorado State University

We recently developed a surface modification strategy that renders asymmetric polymeric membranes permanently hydrophilic.@footnote1@ This entails treating asymmetric membranes with a low-temperature plasma to obtain the desired change in wettability. This treatment is quite versatile as polysulfone, polyethersulfone, and polyethylene membranes are completely hydrophilic as a result of plasma treatment. XPS results indicate that the desired change in wettability observed for plasma-treated membranes is a result of implantation of new, more hydrophilic functional groups by plasma treatment; however, little is known about the chemistry occurring on a molecualr level during plasma modification. Hence, we recently began investigating the mechanisms behind hydrophilic modification of asymmetric polymeric membranes. We have determined the gas-phase composition as well as ion and electron densities with optical emission sepctroscopy (OES), Langmuir probe studies and mass spectrometry. We suspect OH radicals, detected in the OES spectrum, are likely the species predominantly responsible for hydrophilic modification of our porous materials. Therefore, we have studied plasma-generated OH radical/surface reactivites with porous polymeric membranes as the substrate of interest by the IRIS (Imaging of Radicals Interacting with Surfaces) method. This technique is uniquely suited to afford chemical information critical to elucidation of the mechanisms responsible for plasma modification of porous materials. We will report OH reactivites at several porous polymeric substrates including asymmetric polysulfone, polyethersulfone, and polyethylene membranes. We will also present correlations drawn from the aforementioned techniques, proposing the role of OH radicals and other plasma-generated species in plasma processing of porous materials. @FootnoteText@ @footnote 1@M. L. Steen, L. Hymas, E. D. Havey and E. R. Fisher, J. Memb. Sci., to be submitted.

2:40pm **PS1-ThA3 The Mechanisms of Anisotropy Control in Plasma Etching Processes***, **L. Vallier,*** CNRS/LTM, France*; G. Cunge,* CEA/LETI, France*; J. Foucher, D. Fuard,* CNRS/LTM, France*; R.L. Inglebert, O. Joubert,* LTM/CNRS, France **INVITED**

Anisotropic plasma etching of microelectronic materials is achieved thanks to the bombardment of energetic ions, allowing the etch directionality to be achieved, and the formation of volatile etch products, through ion-assisted chemical etching reactions. In this talk, we demonstrate that the anisotropy control of an etch process is obtained via the re-deposition of heavy non-volatile etch products on the feature sidewalls. Experiments have been conducted on a very powerful plasma etch system dedicated to advanced studies. It consists in a Decoupled Plasma Source (DPS) from Applied Materials modified to host in situ diagnostics such as UV-visible ellipsometry, mass spectrometry, fast injection Langmuir probe and X-ray photoelectron spectroscopy (XPS). Etch processes have been developed for silicon gates, low k polymers as intermetal dielectrics and Aluminum as metal for interconnect. Strong correlations have been observed between sidewall passivation layer formation (analyzed by XPS), profile control (through SEM inspection) and etch products analyses (using mass spectrometry analyses). For each material investigated, we have observed that the anisotropy control is only achieved if a passivation layer is formed on the feature sidewalls. At the same time, ion mass spectra clearly shows the presence of non-volatile species: heavy carbon chains for low k polymer etching, and silicon oxide and their derivatives for silicon etching. Mass spectrometric results also indicate that the number density of theses species is varying as the square root of ion energy (DC bias), suggesting that they are produced by the sputtering of the reactive layers formed at the bottom of the etched features. Finally, these experiments show that passivation layers can be designed by tuning the etch product formation. An example of sidewall passivation engineering for poly gate etching will be shown with the formation of a controlled notched profile.

3:20pm **PS1-ThA5 Pulsed Plasma Polymerisation of Acrylic Acid***, **S. Fraser,** D.B. Haddow, R.D. Short,* University of Sheffield, UK

The synthesis of thin plasma polymer films from radio frequency sustained glow discharges of small organic compounds is well documented. Films containing a high degree of retention of the starting monomers original functionality and structure can be deposited using a low power plasma. These plasmas can be sustained by continuous wave (CW) or by pulsing a higher input power to achieve a lower average power. Although there is substantial literature on the use of pulsed plasmas there has not been any investigation made of the pulsed rf plasma environment of monomers containing C, H, O, or N. We describe the application of mass spectrometry and ion energy analysis to probe the pulsed plasma environment of acrylic acid. Analysis of the deposited films was carried out by XPS. The input power was fixed at 50W and the effect of plasma off time was investigated with respect to a fixed on time (eg 5ms/40ms=11% duty cycle). In terms of functional group retention the pulsed 50W plasma at a duty cycle of 11% is equivalent to a 3-3.5W CW plasma. It was shown that in the pulsed plasma the amount of intact acrylic acid was greatly reduced. There is no evidence in the pulsed plasma gas phase neutrals for significant radical-neutral or radical-radical combination. Any neutral species detected can be explained by homolytic cleavage of the carboxyl group and subsequent addition or loss of H. The positive ion mass spectrum of the pulsed acrylic acid plasma shows extensive gas phase oligomerisation was detected. This oligomerisation has been previously described in low power CW plasmas of acrylic acid. The similarities between pulsed 50W and 5W CW plasmas include gas phase chemistry, plasma polymer chemistry and deposition rates. This might suggest that the pulsed plasma environment is a continuation of the low power CW environment, but to lower average

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

powers than can be sustained using a CW signal generator. Measurements of ion energies suggest a more complex system.

3:40pm **PS1-ThA6 Control of Ion Energies in RF Plasmas used for the Surface Modification of Polymers*, D. Barton,*** UMIST, UK*; J.W. Bradley,* UMIST, UK, U.K.*; D.A. Steele, R.D. Short,* University of Sheffield, UK

Despite the widespread use of low pressure (~10mTorr) radio frequency (13.56MHz) plasmas for the surface modification of polymers the importance of the various plasma species, e.g. positive ions and VUV photons, in effecting these changes remains the subject of some debate. To investigate the role of positive ions in the argon plasma treatments of various polymers, we have developed a technique which allows for the in situ control of the ion energies at the polymer surface. The technique does not perturb the bulk plasma, and in particular leaves the VUV flux unchanged. A further advantage is that that no grids or optical windows are placed in front of the sample. The technique is similar in principle to the active compensation of Langmuir probes, in that it relies on feeding an RF signal onto the polymer which is phase and amplitude matched to the (RF) sheath potentials. By increasing the amplitude of this signal, we force the self-bias potential of the sample more positive and thereby reduce the ion energy at the polymer surface. This contrasts with the well known technique of biasing substrates with an unmatched RF signal which greatly increases ion energy to the surface. By varying the contribution from positive ions to the total energy deposition on the polymer surface, we are able to estimate the respective roles of ions and VUV in the surface modification of polystyrene, an important biomedical plastic. The effects of plasma exposure are measured by X-ray photoelectron spectroscopy, XPS. Although demonstrated for a particular plasma reactor, polymer and gas, the approach is generic and could be applied more widely.

4:00pm **PS1-ThA7 Surface Chemical Patterning by Plasma Polymerization*, R.D. Short,*** *N. Bullett, A.J. Beck,* University of Sheffield, UK*; C. Blomfield,* Kratos Analytical, UK

Plasma polymerization has been used to create chemically-patterned surfaces. The fidelity of the patterns is demonstrated by means of imaging TOFSIMS and XPS. The sequential plasma deposition of a hydrocarbon compound (1,7 octadiene) and a functionalized compound (allyl amine or acrylic acid) through electron microscope grids has been used to create surface patterns of amine and carboxyl, respectively, on polymer sheets. By this approach it has been possible to fabricated surfaces containing stripes of 75-150 microns and squares, of similar dimensions, of amine and carboxyl functionalities. These patterns have been used to spatially control protein adsorption, demonstrated using a fluorescent marker, and cell attachment and spreading.

4:20pm **PS1-ThA8 The Relationship between Deprotection and Film Thickness Loss during Plasma Etching of Chemically Amplified Resists*, A.P. Mahorowala,*** *D.R. Medeiros,* IBM T.J. Watson Research Center

Positive-tone chemically amplified (CA) resists provide the sensitivity, contrast and resolution necessary to print state-of-the-art sub-wavelength features using KrF (248 nm) and more recently ArF (193 nm) lithography. These materials are also being looked at for printing sub-100 nm features with F@sub 2@ (157 nm) and next-generation lithography technologies such as EUV (13 nm) and E-beam projection lithography (EPL). Beyond the desired exposure-induced reactions, the acid-catalyzed deprotection reactions responsible for the solubility differential can also occur in unexposed resist areas when etched in a plasma due to uv-exposure, high energy ion bombardment, plasma composition and elevated substrate temperatures. Deprotection has been associated with resist mass loss and film shrinkage during plasma etch that can adversely affect the tight resist budget. In this paper, we determine the film thickness loss during etching of several unexposed CA resists in a variety of plasmas while simultaneously monitoring the film composition by FTIR. These results will be compared with theoretical predictions based on well-known deprotection mechanisms. It will be demonstrated that the acidic nature of certain plasmas such as Cl@sub 2@/O@sub 2@ can deprotect the resist film even in the absence of a photoacid generator (PAG). It will also be shown that the nature of the resist polymer and the identity of the deprotection products directly influence resist mass loss and etch rate linearity both of which can be controlled by careful selection of resist materials.

4:40pm **PS1-ThA9 Study of Defects Induced on Graphite Surface by Low Pressure Argon Plasma*, A.L. Thomann,*** *P. Brault,* GREMI (CNRS), France*; H. Estrade-Szwarckopf, B. Rousseau,* CRMD (CNRS), France*; C. Andreazza-Vignolle, P. Andreazza,* CRMD (Universite d'Orleans), France

Since several years, we have been studying ultra-thin metal film deposition by a plasma sputtering method giving rise to low deposition rates (< 5 Å/min). Previous works have shown that the metal growth mode depends on the deposition conditions, which are tailored by the plasma conditions. For example, Pd metal has been found to form either 3D nanometer clusters, or very thin continuous layers.@footnote 1@ These results are interesting because they evidence that, with this deposition method, the film morphology may be easily chosen for a given application. Our aim is now to study how argon plasma pretreatment may modify the substrate surface state and thus, change growth modes. This will lead to an integrated plasma process allowing surface preparation followed by metal deposition. To study the induced defects, a plasma reactor has been added to an UHV-chamber equipped with STM, AFM, XPS and UPS analyses. This system allows chemical, electronic and morphological characterizations of the substrates before and after plasma treatments of different durations (30 s to 1 h). For these experiments, Highly Oriented Pyrolytic Graphite (HOPG) substrate has been used because it has been thoroughly studied as well as the surface defects created by ions beam techniques. First results show that small (D= some Å) and large (D= tens of Å) size defects are created on HOPG surface, that appear on STM images as hillocks of some Å height. Close to the large defects, a graphite lattice superstructure is observed. After a long lasting plasma treatment, the C1s XPS spectrum of the HOPG surface is completely modified ; on STM images, the hexagonal lattice is no longer observed and the superficial atomic structure appears as highly distorted although with a very small roughness (< 2 Å). @FootnoteText@ @footnote 1@ P. BRAULT et al, Recent Research Development in Vacuum Sci. And Technol., 2, R.A. Gottscho R.J. Pearton Eds. (Transworld Research Network, India, 1000).

5:00pm **PS1-ThA10 Novel Technique to Enhance Etch Selectivity of Carbon ARC over PR based on O@sub 2@/CHF@sub 3@/Ar Gas Chemistry*, J. Hong,*** *J.S. Jeon, Y.B. Kim,* Samsung Electronics, South Korea*; T.-H. Ahn,* Samsung Electronics, South Korea, Korea

New Anti-Reflective Coating (ARC), amorphous carbon (C-ARC) substitute for inorganic ARC (SiON) is gaining attention recently in DRAM process as device scales down requiring more fine control of submicron (0.8) was achieved with annealing of amorphous carbon. The presence of hydrogen radical in the plasma produced similar result with C-ARC phase transition from sp@sub 3@ to sp@sub 2@ resulting from hydrogen-hydrogen abstract reaction. Deposition temperature of C-ARC determined hydrogen content on the surface. Hydrogen behavior on the surface appeared to be dominant factor to control etch selectivity and surface reaction mechanism of amorphous carbon will be discussed.

Plasma Science and Technology
Room 311 - Session PS2-ThA

Dielectrics I

Moderator: J.L. Cecchi, University of New Mexico

2:00pm **PS2-ThA1 Ion Energy Control for Enhanced Plasma Etch Selectivity*, Y. Andrew,*** *E. Ko, J. Machima, S.-B. Wang, A.E. Wendt,* University of Wisconsin, Madison

Ion energy distribution (IED) control@footnote1@ at the substrate during plasma etching has been examined for improvements in SiO@sub 2@/Si and SiO@sub 2@/photoresist etch selectivity. The IED is controlled using a tailored bias voltage waveform applied to the substrate in place of the conventional RF sinusoidal waveform. A periodic waveform consisting of a voltage ramp in combination with a short pulse produces a plasma sheath in front of the wafer with nearly time-invariant voltage, leading to a nearly monoenergetic ion flux at the substrate, as compared to the relatively broad IED typically produced by a sinusoidal waveform. A 13.56 MHz helicon etching tool, equipped with a substrate bias power supply capable of producing the tailored substrate bias waveform, has been used to etch blanket films of photoresist, Si and SiO@sub 2@ using sinusoidal and tailored bias voltage waveforms. Etch rates of the blanket films are measured in situ using laser interferometry. Results to be presented show improved selectivity with the tailored waveform and a broadened process window for selective etching of SiO@sub 2@ over silicon in fluorocarbon-based plasmas, and etch rate vs. ion energy data suggest physical mechanisms. Selective etching of SiO@sub 2@ over photoresist is also examined, as it is very desirable to reduce the demand for thick photoresist and the challenge it presents to lithography technology. Substantial improvements in SiO@sub 2@/photoresist selectivity are expected. @FootnoteText@@footnote 1@S. B. Wang and A.E. Wendt, "Control of ion-energy distribution at substrates during plasma processing" to be published, J. Appl. Phys., June 1999.

2:20pm **PS2-ThA2 Temperature and Bias Effects in ICP Etching of Silicon Dioxide***, **M.J. Cooke**, G. Hassall,* Oxford Instruments Plasma Technology Ltd., UK

Silicon dioxide etching has been evaluated in a new induction-coupled plasma (ICP) source (designated ICP380), with particular attention to the sources of nonuniformity in etching 200 mm wafers. The contributions of the ICP source, the rf bias to the wafer, and the gas flow distribution to uniform etching are examined experimentally, supported by simple models. The implications for the design of etching hardware and for the protocols to achieve reproducible processes are considered. The rate of polymer deposition and etching in fluorocarbon plasmas has been measured as a function of the ion impact energy and the temperature of the substrate, using interferometry and direct film thickness measurements. This has been related to the etch profile evolution for 10 micron deep trenches in thick silicon dioxide layers. It is shown that substrate temperature control is a necessary part of profile control, even for etches which are normally considered to be regulated by ion bombardment.

2:40pm **PS2-ThA3 Control of Incident Fluxes and Surface Reactions in the Etching of Dielectric Materials***, **T. Tatsumi**, M. Matsui, K. Kinoshita, S. Kobayashi, M. Sekine,* Association of Super-Advanced Electronics Technologies (ASET), Japan

The relationship between SiO@sub 2@ etch rates and the incident flux of reactive species in dual-frequency (27/0.8 and 60/2 MHz) parallel-plate systems were evaluated by using various in-situ measurements tools, such as infrared IRLAS, QMS, and OES. The thickness of a C-F polymer layer on the etched SiO@sub 2@ surface was measured by XPS. The SiO@sub 2@ etch rate depends on both the total amount of F in the C-F reactive species and the ion energy at a reactive layer on the SiO@sub 2@ surface.@super 1@ The net energy supplied to the reactive layer depends on the total amount of ions, the acceleration energy of ions (assumed to be the peak-to-peak voltage, V@sub pp@), and the energy loss in the C-F polymer layer. The C-F polymer thickness increased when the incident flux of C-F species was relatively higher than the removal ability of C-F polymer, that mostly depends on oxygen flux. To vary the incident CF@sub x@ species, the C@sub 4@F@sub 8@ flow rate in the C@sub 4@F@sub 8@/Ar/O@sub 2@ was increased under 30mTorr of gas pressure and 1450 V of V@sub pp@. The ion flux was controlled by adjusting the RF powers. When we increased the ion flux from 3.0 x 10@super 16@ to 3.6 x 10@super 16@ cm@super -2@s@super -1@, the etch rate was increased because the energy on the reactive layer increased while the Si etch rate remained the same. Furthermore, the formation of the thick polymer (>1nm) started under higher C@sub 4@F@sub 8@ flow-rate conditions. This means the ability to remove excess C-F polymer on the etched surface was also improved. As a result the process-window of selective etching was increased. C@sub 5@F@sub 8@/Ar/O@sub 2@ gas chemistry was also evaluated in the same manner. An increase of C-concentration of the parent gas molecules induces the excess incidence of C atoms to the surface. As a result we mostly observed the C-F polymer deposition rate (not steady-state thickness) under high C@sub 5@F@sub 8@ flow-rate conditions. It is necessary to use the lower pressure or higher ion energy conditions to suppress the excess formation of the C-F polymer in the C@sub 5@F@sub 8@/Ar/O@sub 2@ process. @FootnoteText@ This work was supported by NEDO. @footnote 1@T.Tatsumi et al., J. Vac. Sci. Technol., A17 (1999) 1562.

3:00pm **PS2-ThA4 Reaction Mechanisms and SiO@sub 2@ Profile Evolution in Fluorocarbon Plasmas: Bowing and Tapering@footnote 1@***, **D. Zhang**,* University of Illinois at Urbana-Champaign*; C. Cui,* Applied Materials, Inc.*; M.J. Kushner,* University of Illinois at Urbana-Champaign

The rate and quality of fluorocarbon plasma etching of dielectrics is largely determined by a balance between deposition of polymer and ion activated chemical or physical sputtering. The proper balance results in selectivity and sidewall passivation producing straight walled features. The scaling of SiO@sub 2@ etching in fluorocarbon plasmas was numerically investigated using the Hybrid Plasma Equipment Model and the Monte Carlo Feature Profile Model (MCFPM). Algorithms were added to Surface Kinetics Module to account for multiple polymer layers, delivery of activation energy through polymer layers and ion activated polymer deposition. The MCFPM was also improved by including these processes. Reaction mechanisms were developed in which deposition of C@sub n@F@sub m@ radicals, either direct or ion activated, produces a polymer layer. At the interface of the polymer layer and SiO@sub 2@, a C@sub n@F@sub m@-SiO@sub 2@ complex is formed which, in the presence of fluorination by F atoms diffusing and ion energy delivery through polymer layers, produces etching in a 2 step process. Selectivity to Si results from lack of consumption of the polymer layer. SiO@sub 2@ etch rates increase with increasing bias at low biases due to increased activation energy delivered through a thinner passivation layer. Etch rates saturate at high biases due to polymer starvation. Comparisons to experiments showed that etch profiles transitioned from bowed to tapered as the passivation flux to ion flux ratio increased. This transition is delayed to higher passivation flux to ion flux ratios by increasing the bias. In general, loss of critical dimension correlated with a reduction in etch rate due to the thickening of passivation layers. For this reason, saturation of the etch rate due to polymer starvation also improved maintenance of the critical dimension. @FootnoteText@ @footnote 1@Work supported by AMAT, LAM, SRC and NSF.

3:20pm **PS2-ThA5 Etching Mechanism of Silicon Nitride Film in Self-aligned Contact Etching Process***, **M. Ito**, S. Senda, K. Kamiya, M. Hori, T. Goto,* Nagoya University, Japan

For a contact hole etching process, the high etching selectivity of SiO@sub 2@ over Si@sub 3@N@sub 4@ as well as Si is required. In order to clarify the etching mechanism of Si@sub 3@N@sub 4@ film in H@sub 2@ diluted C@sub 4@F@sub 8@/Ar electron cyclotron resonance plasmas, we have investigated the mixing-layer in Si@sub 3@N@sub 4@ films using in-situ X-ray photoemission spectroscopy and in-situ Fourier transform-infrared reflection absorption spectroscopy. From etching results and C-N bonding compositions in the mixing layer as a function of H@sub 2@ dilution ratio, the intensities of C-N sp@super 2@ bonds are considered to have a relation with the etching rate of Si@sub 3@N@sub 4@. On the other hand, C-N sp@super 1@ bonds were not observed at all in the films. Moreover, to clarify the H@sub 2@ dilution effect, we have observed the surface reaction during H@sub 2@ plasma annealing after etching Si@sub 3@N@sub 4@ films under C@sub 4@F@sub 8@/Ar plasma condition. It was found that intensities of C-N sp@super 2@ bonds as well as sp@super 3@ bonds decreased while Si-N bonds increased with the annealing time. Therefore, C-N sp@super 2@ bonds as well as C-N sp@super 3@ bonds are suggested to be etched through the formation of byproduct such as HCN and to be broken to form Si-N bonds through the recombination of the dangling bonds such as -N and -Si. This fact suggests that the restriction of reaction of C-N sp@super 2@ bonds and C-N sp@super 3@ bonds with H or F atoms is a key factor for achieving higher selective etching of SiO@sub 2@ over Si@sub 3@N@sub 4@.

3:40pm **PS2-ThA6 High-performance Silicon Dioxide Etching for High-aspect Contact Holes***, **S. Samukawa**,* NEC Corp., Japan **INVITED**

SiO@sub 2@ etching is done by using fluorocarbon gases to deposit a fluoropolymer on the underlying silicon. This deposit enhances the etching selectivity of SiO2 over silicon or silicon nitride. CF@sub 2@ radicals especially are used as the main gas precursor for polymer deposition. In a conventional gas plasma, however, the CF@sub 2@ radicals and other radicals (high-molecular-weight-radicals: C@sub x@F@sub y@) lead to the polymerization. This condition causes microloading and etching-stop in high-aspect-contact hole patterning due to the sidewall polymerization during SiO@sub 2@ etching processes. Conversely, by new fluorocarbon gas chemistries (C@sub 2@F@sub 4@/CF@sub 3@I), we achieved selective radical generation of CF2 and eliminated high-molecular-weight-radicals. Under this condition, microloading-free and etching-stop-free high-aspect-ratio-contact-holes patterning of SiO@sub 2@ was accomplished. Thus, the higher molecular weight radicals play an important role in the sidewall polymerization in contact holes because these radicals have a higher sticking coefficient than CF@sub 2@ radicals. Selective generation of CF@sub 2@ radicals and suppression of C@sub x@F@sub y@ radicals are thus necessary to eliminate the microloading and etching-stop when formation high-aspect-contact-ratio holes.

4:20pm **PS2-ThA8 Selective Etching of SiO@sub 2@ in High Density Fluorocarbon Plasmas for Applications in Micro-systems***, F. Gaboriau, M.-C. Peignon, G. Turban, **Ch. Cardinaud**,* CNRS-University of Nantes, France

In the recent years, plasma processes using high density sources have been extensively developed to meet the more and more stringent constraints required by integrated circuits fabrication. Among the various steps, dielectric etching is the more challenging as processes rely on polymerizing hydrofluorocarbon gases that produce simultaneously deposition and etching. It is thus difficult to achieve adequate SiO@sub 2@/mask etch selectivity and to continue etching in high aspect ratio features at the same time. Our aim is to develop new plasma processes concerning the oxide etching step for micro-machining device elaboration. Fabrication of MEMS (micro electro mechanical systems) and O-MEMS (optical MEMS) requires several conditions : i) a higher etch rate, ii) an extreme selectivity, iii) much longer etching processes. Previous studies have shown that adding methane to a fluorocarbon gas (CHF@sub 3@, C@sub 2@F@sub 6@, CF@sub 4@) yields to a significant improvement of the selectivity from 4 to 20 with no significant loss in the SiO@sub 2@ etch rate (300 nm/min). The present study using in-situ real time measurements by ellipsometry and quasi in-situ XPS analysis is focused on the influence of gas flow rate on the SiO@sub 2@ and Si (acting as a mask) etching using a mixture C@sub 2@F@sub 6@-CH@sub 4@. C@sub 2@F@sub 6@ was chosen due to a higher oxide etch rate compared to CHF@sub 3@ and CF@sub 4@. Increasing the gas flow rate when using pure C@sub 2@F@sub 6@ yields to an increase of both material etch rates ; the selectivity is thus unchanged and equal to 2. In contrast, using C@sub 2@F@sub 6@-CH@sub 4@ mixtures with 40% of methane leads to a significant improvement of the selectivity (from 4 to 15) when increasing total gas flow rate ; indeed, oxide etch rate shows the same behavior as before whereas silicon etch rate decreases when increasing gas flow rate. Besides, XPS analysis exhibits a dependence between the silicon etch rate and the fluorocarbon layer thickness pointing out that this overlayer controls the silicon etching. Influence of the gas flow rate on the gas phase is under study using mass spectrometry, optical emission spectroscopy and Langmuir probe ; these diagnostics will allow us to determine the ion flux on the surface and to correlate the different evolutions of plasma species with the etch rate evolution for a better understanding of SiO@sub 2@ and Si etch mechanisms.

5:00pm **PS2-ThA10 Trench Etch Processes for Dual Damascene Patterning of Low-k Dielectrics***, **P. Jiang**, F.G. Celii, W.W. Dostalik, K.J. Newton,* Texas Instruments, Inc.*; H. Sakima,* Tokyo Electron America

The use of dual damascene patterning for integration of Cu with low-k dielectric films has introduced new challenges for plasma etch processes. With a via-first dual damascene approach, an important issue for trench etch is defect formation (i.e., oxide ridges) around vias which can degrade device reliability. The use of low-k films as the dielectric material adds additional complexity and more limitation on the etch process parameters. This paper discusses the development of etch processes that meet the special requirements for Cu/low-k dual damascene trench etch. All experiments were conducted in a medium-density TEL Dipole Ring Magnetron (DRM) system. The dielectric film used here was an organosilicate glass (OSG). Using C@sub 4@F@sub 8@/N@sub 2@/Ar chemistry, a trade-off was observed between etch rate and oxide ridge formation. The N@sub 2@/Ar ratio was found to be the key parameter in controlling the severity of the oxide ridges, but eliminating the ridges using the N@sub 2@/Ar ratio resulted in a low OSG etch rate and poor throughput. However, we will discuss an alternative method which achieves high OSG etch rate while maintaining CD control and ridge-free conditions. The effect of various process parameters on the OSG etch rate and ridge formation will be detailed. A comparison of experimental results against numerical simulations of C@sub 4@F@sub 8@-based bulk plasmas with varying gas flow ratios will also be reported.

Semiconductors
Room 306 - Session SC+SS+EL-ThA
III-Nitride Growth and Nucleation

Moderator: V.M. Bermudez, Naval Research Laboratory

2:00pm **SC+SS+EL-ThA1 Kinetics of GaN Growth and Decomposition***, **D.D. Koleske**, A.E. Wickenden, R.L. Henry, M.E. Twigg, J.C. Culbertson,* Naval Research Laboratory **INVITED**

While many devices have been demonstrated in the group III nitrides, details of the chemical reaction mechanisms for producing high quality GaN using metallorganic vapor phase epitaxy (MOVPE) continues to be an active area of research. In this presentation, I will highlight the results from several kinetic studies of GaN growth. This will include investigations of GaN decomposition in a commercial MOVPE reactor at temperatures and pressures typically used for growth. The GaN decomposition rates were measured in H@sub 2@, N@sub 2@, mixed H@sub 2@ and N@sub 2@, and mixed H@sub 2@ and NH@sub 3@. From these studies an enhancement in the GaN decomposition rate is observed in pure H@sub 2@ and mixed H@sub 2@ and NH@sub 3@ flows as the reactor pressure is increased above 100 torr. @footnote 1@ The mechanism for enhanced GaN decomposition will be presented. Measurements of GaN growth (with trimethylgallium) and decomposition (without trimethylgallium) rates under otherwise identical conditions indicate the extent of decomposition and incorporation during growth. GaN decomposition also accounts for a decrease in the GaN nucleation at higher pressures during the initial high temperature growth. This decrease in the nucleation density leads to increased grain size and higher quality GaN films.@footnote 2@ Kinetic issues relating to incorporation of defects will also be presented. These issues include a growth model for stoichiometric GaN growth,@footnote 3@ and the kinetics of surface carbon removal. All work sponsored by the Office of Naval Research. @FootnoteText@ @footnote 1@ D.D. Koleske, et al., Appl. Phys. Lett. 73, 2018 (1998); ibid. 75, 1646 (1999). @footnote 2@ A.E. Wickenden, et al., J. Electron. Mat. 29, 21 (2000). @footnote 3@ D.D. Koleske, et al., J. Appl. Phys. 84, 1998 (1998).

2:40pm **SC+SS+EL-ThA3 Carbonization of Si (111) by Gas Source Molecular Beam Epitaxy using Triethyl Gallium and Subsequent GaN Growth***, **E. Kim**, A. Tempez, A. Bensaoula,* University of Houston

Next to sapphire, SiC is the most commonly utilized substrate for GaN heteroepitaxy. In addition to a better lattice match it has the advantage of being available in either conducting or insulating form. The most desirable substrate from both processing and cost point of view is Si since it will allow direct integration of GaN-based devices with conventional Si technology. To that end many approaches have been attempted to overcome the lattice mismatch and nucleation issues for GaN deposition on Si. We have already reported on RF-MBE and chemical beam epitaxy (CBE) of GaN on Si(111) using AlN buffer layers and demonstrated LEDs from our materials. To further improve on our previous results we explored the use of SiC as a buffer layer for the growth of GaN on Si. In this paper we demonstrate deposition of GaN on a SiC buffer layer formed by in situ carbonization of Si using a metalorganic precursor (triethylgallium: TEG) as the carbon source. The carbonization of the Si (111) surface is identified using in-situ time of flight low energy ion scattering, ex-situ XPS and XRD. The thickness, the crystalline quality and the surface morphology of the carbonized layer are found to be very temperature dependent. A 6H-SiC polycrystalline thin film is formed above 780°C. Layers formed at 800°C are thicker and rougher than those formed at 780°C. In either case, Ga is not incorporated into the SiC layer. The SiC layer is shown to efficiently block the formation of SiO@subx@N@suby@ surface species which hinders the GaN nucleation and makes GaN/Si heteroepitaxy non-reproducible. GaN layers deposited in the same reactor by CBE using TEG and ammonia were analyzed as a function of the SiC layer thickness and annealing temperature. Data from these layers as well as from RF-MBE GaN deposited on these SiC buffer layers will also be presented. This project was funded by a NASA cooperative grant #NCC8-127 to the Space Vacuum Epitaxy Center.

3:00pm **SC+SS+EL-ThA4 Epitaxial III-V Nitride Growth on SiC(0001) by Means of A@super 3@@Sigma@@sub u@@super +@ Metastable Molecular Nitrogen***, **D.C. Jordan**, D.J. Smith, I.S.T. Tsong, R.B. Doak,* Arizona State University

High quality epitaxial III-N semiconductor films, ranging in thickness from 300 to 900 Å, have been grown using A@super 3@@Sigma@@sub u@@super +@ metastable nitrogen molecules. The work employed a corona discharge supersonic free-jet (CD-SFJ) to generate a molecular beam containing exclusively the A@super 3@@Sigma@@sub u@@super +@ activation state in an otherwise ground state N@sub 2@ beam. AlN films were grown on 6H-SiC(0001) and Si(001) substrates. GaN films were grown on the same substrates and on buffer layers of AlN deposited in situ on 6H-SiC(0001). The N-atom incorporation efficiency (defined as the number of N-atoms attaching to a III-N surface per incident metastable A@super 3@@Sigma@@sub u@@super +@ molecule) approached 100% in most instances and was found to be independent of substrate temperature from 600 to 900 Â°C, implying direct molecular chemisorption as the underlying reaction mechanism. These measurements support theoretical predictions that A@super 3@@Sigma@@sub u@@super +@ is an ideal precursor for III-N growth.

3:20pm **SC+SS+EL-ThA5 Crystal Growth Kinetics and Transport in GaN Epitaxial Lateral Overgrowth***, **M.E. Coltrin**, C.C. Willan, M.E. Bartram,* Sandia National Laboratories **INVITED**

Epitaxial Lateral Overgrowth (ELO) is a useful technique to improve material quality and reduce defects in GaN. In ELO, a mask pattern of dielectric material, usually either silicon nitride or silicon dioxide, is deposited on top of a GaN buffer layer. Further growth of GaN occurs selectively on exposed areas of the underlying buffer layer, and not on the dielectric material. Typically, ELO conditions are optimized for a maximum lateral - to - vertical growth rate ratio. Growth kinetics of GaN crystal faces and transport effects will be discussed in this paper. Dimensions of the exposed and masked areas in line and dot patterns, pattern orientation with respect to the underlying substrate, and growth time were systematically varied. Growth rate information was obtained from scanning electron microscope (SEM) measurements. The coupling between transport and kinetic effects was examined by means of 2-D and 3-D numerical simulations. In general, transport of material from the masked to the unmasked regions is quite efficient. However, ELO deposition growth efficiency is shown to decrease dramatically when the ratio of exposed to masked areas becomes very small. ELO experiments incorporating deep trenches will be described, which are designed to distinguish between lateral transport of material via gas-phase vs. surface diffusion. Gas-phase transport of material appears to dominate. We have found a quantitative way to translate results from different pattern dimensions into a pseudo time basis by scaling growth features by a length scale W, the size of the exposed deposition window.

4:00pm **SC+SS+EL-ThA7 Thick GaN on Si Substrate by Hydride Vapor Phase Epitaxy using Epitaxial Lateral Overgrowth Technique***, **J.W. Lee**, J.B. Yoo,* Sungkyunkwan University, Korea

The thick GaN growth is a very essential issue for the fabrication of GaN substrate. Epitaxial lateral overgrowth (ELOG) is one of the promising techniques for the high quality GaN epilayer as a fabrication of optical and electronic devices. In this study, two-step growth of GaN was optimized to grow high-quality GaN. First, we attempt ELOG technique for growth of GaN on a Si(111) substrate by MOCVD. Then the thick GaN film was overgrown on ELOG GaN by HVPE. Because of their large lattice mismatch between GaN and Si, the use of an intermediate layer or buffer layer is essential. For the growth of GaN on Si substrate the AlN layer was used to buffer layer. The AlN buffer layer was deposited by RF sputtering. The LT-GaN by was induced another buffer layer on Si substrate. The ELOG GaN on Si substrate was grown by MOCVD. The TMGa and ammonia were used as source gases. The growth temperature of ELOG GaN was changed range in 500°C to 1100°C. The thick GaN was grown by conventional HVPE. The chlorinated gallium and ammonia were used as source gas for Ga and N, respectively. The growth temperature of thick GaN was varied from 800°C to 1100°C. The SiO@sub 2@ was grown by PECVD for the use of ELOG mask on buffer layers. The stripe pattern was developed along and crystal axis of GaN. The various stripe windows with a different spacing between stripes were developed on the SiO@sub 2@ mask by conventional photolithography and wet chemical etching. The effect of growth parameters such as AlN, LT-GaN, growth temperature, stripe patterned direction were investigated. Surface roughness and morphologies of ELOG GaN film were analyzed by atomic force microscopy (AFM) and scanning electron microscope (SEM). The effect of ELOG on thick GaN-film was characterized by double crystal x-ray diffractometer (DCXRD), low temperature photoluminescence (PL) and transmission electron microscope (TEM).

4:20pm **SC+SS+EL-ThA8 Growth and Electronic Structure of ScN, a New Refractory III-V Semiconductor***, **D. Gall**, I. Petrov, J.E. Greene,* University of Illinois, Urbana

ScN layers, 40 to 345 nm thick, were grown on MgO(001) substrates at 750 °C by ultra-high-vacuum reactive unbalanced magnetron sputter deposition in pure N@sub 2@ discharges at 5 mTorr. All films were stoichiometric with N/Sc ratios of 1.00±0.02. Microstructural and surface morphological evolution were found to depend strongly on the energy E@sub i@ of N@sub 2@@super +@ ions incident at the film surface during deposition. Nucleation and the initial growth of ScN layers deposited with E@sub i@ = 13 eV are dominated by the formation of 111 and 002-oriented islands which exhibit local epitaxy. However, preferred orientation rapidly evolves toward a purely 111 texture by a film thickness of ~50 nm as 002 grains grow out of existence in a kinetically-limited competitive growth mode. In distinct contrast, ScN layers deposited with E@sub i@ = 20 eV are single crystals which grow in a cube-on-cube epitaxial relationship with MgO(001). ScN optical properties were determined by transmission, reflection, and spectroscopic ellipsometry while in-situ x-ray and UV valence-band photoelectron spectroscopy were used to determine the density of states (DOS) below the Fermi level. The measured DOS exhibits peaks at 3.8 and 5.2 eV stemming from the N 2p bands and at 15.3 eV due to the N 2s bands. The imaginary part of the measured dielectric function @epsilon@@sub 2@ consists of two primary features due to direct X- and @GAMMA@-point transitions at photon energies of 2.7 and 3.8 eV, respectively. The ScN band structure was calculated using an ab initio Kohn-Sham approach which treats the exchange interactions exactly within density-functional theory. Combining experimental and computational results, we show that ScN is a semiconductor with an indirect @GAMMA@-X bandgap of 1.3±0.3 eV and a direct X-point gap of 2.4±0.3 eV.

4:40pm **SC+SS+EL-ThA9 Structure and Optical Properties of ScN(001) Grown by Molecular Beam Epitaxy***, **H. Al-Brithen**, A.R. Smith, W.M. Jadwisienczak, H.J. Lozykowski,* Ohio University

Scandium nitride is grown by molecular beam epitaxy on MgO(001) substrates. Reflection high energy electron diffraction and x-ray diffraction both confirm the (001)-orientation of the ScN layer. The measured lattice constant is in close agreement with the expected lattice constant a = 4.501 Å, and there is no sign of strain aside from that due to differential thermal contraction between film and substrate during cooling. As measured by atomic force microscopy and scanning tunneling microscopy (STM), these films are found to be smooth, with terraces separated by steps of height a/2. As the Sc flux is varied, the growth morphology also varies - from that of plateaus and pyramids (for lower Sc flux) to that of spiral mounds (for higher Sc flux). We associate the transition with a particular ratio of Sc flux to N flux. Films grown with a lower Sc/N flux ratio have a distinct reddish appearance, and a turn-on feature at 570 nm in the cathodoluminescence (CL) spectrum is measured, consistent with a band gap energy of about 2.2 eV. Films grown with higher Sc/N flux ratio are dark in appearance, and no turn-on feature at 570 nm is observed in the CL spectrum. STM images atomically resolve the rock-salt surface lattice for films grown with lower Sc/N flux ratios; however, for films of higher Sc/N flux ratio, small protrusions are observed on the terraces, which are most likely excess Sc atoms. The effect of the Sc/N flux ratio on the stoichiometry of the films will also be discussed.

5:00pm **SC+SS+EL-ThA10 ScN Thin Films and Thin Film Devices***, **X. Bai**, M.E. Kordesch,* Ohio University

ScN films have been grown by plasma assisted physical vapor deposition (PAPVD) and reactive sputtering on quartz, sapphire, silicon and MgO. Growth temperature ranges from 300K to 1100K, thickness ranges from 50nm to 800nm. For PAPVD films, the XRD results show that ScN grows with (111) texture on quartz, both ScN (111) and (200) textures are observed on sapphire (0001), and (200) textured growth on Si (100). ScN films grown at 300 K are amorphous. Sputtered films show both (111) and (200) texture under various conditions. ScN grows epitaxially on MgO (100). Measurement of the lattice constant ranges from 0.442 nm on quartz to 0.458 nm on silicon. Temperature dependent condcutivity measurements show that ScN is a semiconductor. Intrinsic, p type and n type ScN can be synthesized, with carrier concentrations between 10@super12@ cm@super-3@ to 10@super22@cm@super-3@. The index of refraction is determined from IR measurements to be 2.46 ± 5%. The best optical bandgap result from our measurements is 2.26 eV. There are theoretical predictions of an indirect gap at about 1 eV, outside of our measurement range. ScN films have been used to fabricate p-n junctions, junctions with p and n type Si, and lattice mismatched isotype n-n junction with GaN. Functional ohmic contacts to ScN have been fabricated using Ti, Pd and Ni.

Surface Science
Room 208 - Session SS1+MC-ThA
Oxidation and Molecule-Oxide Interactions

Moderator: S.A. Joyce, Pacific Northwest National Laboratory

2:00pm **SS1+MC-ThA1 Real Time TEM Observations of the Oxidation of Silicon***, **F.M. Ross**,* IBM Research Division **INVITED**

By making real-time observations of the progressive changes occurring at the silicon/oxide interface during oxidation, it is possible to examine the mechanism of the reaction and accurately measure the oxidation kinetics. In this presentation we will describe experiments carried out in a UHV transmission electron microscope which has been modified to allow images to be obtained before, during and after oxidation. By careful choice of imaging conditions we can follow the motion of the silicon/oxide interface in real time during oxidation, and in particular we can observe the configuration of interface steps. Our experiments show that passive oxidation, in which SiO@sub 2@ is formed, occurs in a layer-by-layer fashion with no flow of interface steps. Active oxidation is also a terrace reaction, although the SiO which is formed evaporates preferentially from surface steps. We will briefly discuss how the observation and analysis of step and terrace contrast is a powerful tool for examining the mechanism of other silicon surface reactions, such as epitaxial growth or silicide formation, as well as oxidation.

2:40pm **SS1+MC-ThA3 Comparison of Electrochemical Corrosion Properties and Oxidation Kinetics of Ozone- and Oxygen-formed Aluminum Oxide Films***, **A. Kuznetsova**, I. Popova, V. Zhukov, G. Zhou, J.C. Yang, J.T. Yates, Jr,* University of Pittsburgh

Ozone, O@sub 3@, has been employed to produce an aluminum oxide layer (thickness about 20 Å), on Al(111)and also on polycrystalline Al surfaces. It has been found, by electrochemical impedance spectroscopy, that the impedance of such films is about 10 times higher than films grown to similar thickness with O@sub 2@.Transmission electron microscopy studies have shown that the average pore size of Al@sub 2@O@sub 3@ films grown with O@sub 3@ (20 Å) is smaller than in films grown with O@sub 2@ (100 Å). In addition, electron diffraction studies of amorphous film have shown that the density of oxide film grown with O@sub 3@ is 10% greater than for oxide films grown with O@sub 2@. Thus the enhanced corrosion passivation properties of O@sub 3@-grown aluminum oxide films may be caused by the reduction of defect site density when O@sub 3@ is used.

3:00pm **SS1+MC-ThA4 Temperature Dependent Adsorption of Oxygen on TiO@sub 2@ (110): A Photoemission Study***, **H. Geisler**,* Xavier University of Louisiana*; E.L.D. Hebenstreit, W. Hebenstreit, M. Li, U. Diebold,* Tulane University*; S.N. Thornburg, C.A. Ventrice, Jr.,* University of New Orleans*; D.A. Hite, P.T. Sprunger,* CAMD/ Louisiana State University

The Titanium dioxide (110) surface is one of the most thoroughly studied metal oxide systems. One of the primary reasons for this interest is the fact that TiO@sub 2@ is easily reduced by annealing in vacuum. During the annealing process, oxygen vacancies and titanium interstitial are created, which can increase the conductivity of the substrate sufficiently to allow characterization with electron and ion spectroscopies. In order to heal the surface region, the reduced crystals are exposed to oxygen at various temperatures and pressures. To determine the effect of oxygen adsorption on the electronic structure of reduced TiO@sub 2@ crystals, angular resolved photoelectron spectroscopy (UPS) measurements have been performed in conjunction with scanning tunneling microscopy (STM) measurements. STM indicates that the adsorption of oxygen on TiO@sub 2@ (110) at temperatures above 400 °C or below 200 °C results in an unreconstructed surface. However, adsorption between 200 °C and 400 °C results in a rosette-like structure that represents an incomplete restructured TiO@sub 2@ (110) surface with coordinatively unsaturated surface atoms.@footnote 1@ UPS measurements of the vacuum-annealed, reduced TiO@sub 2@ surface show emission from a defect state centered at approximately 1 eV below the Fermi level. The onset of emission from the TiO@sub 2@ valence band occurs ~3 eV below the Fermi level. After dosing oxygen at room temperature the defect state disappears with only slight modifications to the valence band structure. On the other hand, UPS spectra from the rosette- structured surface show an enhancement of the emission from the defect state and strong modifications of the TiO@sub 2@ valence band emissions. @FootnoteText@@footnote 1@ M. Li, W. Hebenstreit, L. Gross, et al., Surf. Sci. 437, 173-190 (1999)

3:20pm **SS1+MC-ThA5 Water Reactions at Plutonium Oxide: Surface Chemistry***, **J.D. Farr**, R.K. Schulze, M.P. Neu, L.A. Morales,* Los Alamos National Laboratory

We have examined the surface chemistry of water at both monolithic and high surface area plutonium oxide using Auger and X-ray photelectron spectroscopy (AES and XPS). This work investigates the chemical reactions at the Pu oxide surfaces, primarily to help address issues that are critical for plutonium stabilization and 50-year storage. Interactions between PuO@sub 2@ particles and the adsorbed water vapor play a dominant role in potential catalytic gas generation reactions. Understanding the chemistry at this interface, particularly with respect to reactions with water and water vapor is crucial for predicting the storage behavior of Pu oxide powders. XPS indicates that water adsorbs initially at active sites to form surface hydroxyls groups. Upon saturation of these sites and at substantially higher exposures, particularly with high surface area oxides, the water adsorbs in molecular form as part of the surface layer. Heating the oxide to 200°C in vacuum results in removal of the adsorbed water and partial removal (conversion) of the hydroxyl. Above 400°C the oxide surface continues to undergo a transformation and the removal of hydroxyl is largely complete at 600°C. The tenacious nature of these surface groups suggests that most of the active sites at the surface are irreversibly saturated at room temperature and up to a temperature in excess of 200°C, with some of them irreversibly saturated up to 600°C, or greater. The surface reaction will be discussed in the context of reaction energetics for the active sites at the PuO@sub 2@ surface.

3:40pm **SS1+MC-ThA6 Studies of Water Plasma Treatments on Silicon Oxide Films***, **N.A. Alcantar**,* University of California, Santa Barbara*; T.L. Kuhl,* University of California, Davis*; A. Stacy, J. Au, E.S. Aydil, J.N. Israelachvili,* University of California, Santa Barbara

Chemically active oxide surfaces can react with polymers to enhance their surface properties. Surfaces covered with polyethylene glycol have been shown to reject biological attack and protein adhesion. We activate silicon dioxide (i.e., silica) films by exposing them to water vapor plasma. These activated films are then reacted with polyethylene glycol (PEG, OH-(CH@sub 2@-CH@sub 2@-O)@sub n@-H) to make them biocompatible. We have characterized silica films prepared by plasma enhanced chemical vapor deposition (PECVD) before and after water plasma activation. We found that water plasma treatments chemically and physically modify the silica surface. For instance, water plasma fully saturates the silica surface with hydroxyl groups, significantly reduces their surface roughness without affecting the thickness of the deposited films and increases their cohesion force. This surface modification was monitored by in situ real time attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy. Other characterization techniques such as ellipsometry, atomic force microscopy (AFM), surface forces apparatus (SFA) and contact angle measurements were utilized to fully establish the effects of this surface modification. The optimal water plasma parameters for creating smooth, chemically reactive silicon oxide films were also obtained.

4:00pm **SS1+MC-ThA7 The Nature of Oxygen at Rocksalt and Spinel Oxide Surfaces***, **M.A. Langell**, J.G Kim, S. Chapman, H.Y. Xu,* University of Nebraska

The chemical environment of oxygen in mixed metal oxides with compositions M@subx@M'@sub(x-1)@O and M@subx@M'@sub(3x-1)@O@sub4@, (M, M' = Li, Mn, Fe, Ni, Co) has been studied by Auger electron spectroscopy, x-ray photoelectron spectroscopy and high resolution electron energy loss spectroscopy. While there is a single type of lattice oxygen in the bulk structure of simple rocksalt and spinel oxides, the nature of oxygen at the surface of the mixed-metal oxide materials is considerably more complex. Photoemission from core oxygen states in these materials often shows multiple peaks and satellite structure which have been attributed to a range of intrinsic and extrinsic oxygen states. Mixed-metal oxides form an ideal set of systems to investigate the nature of the lattice oxygen through their ability to tailor cation oxidation state and site occupancy within the crystal structure and thus affect the chemical environment of the lattice oxygen. All of these 3d transition metal oxides show a single, intense O1s core photoemission peak at approximately 529.6 eV. However, a second peak is often observed at about 1-1.5 eV higher binding energy, depending upon the types and distribution of the cations, and the history of the substrate surfaces. Surface hydroxylation, cation clustering and final state effects in the photoemission mechanism can all contribute to the O1s photoemission process and will be discussed in view of the data obtained for the mixed-metal oxides.

4:20pm **SS1+MC-ThA8 Direct Observation of Native Hydrogen Adatoms on Rutile TiO@sub 2@(110) Surface***, **T. Fujino**, K. Inudzuka, T. Okuno, M. Katayama, K. Oura,* Osaka University, Japan

Titanium dioxide (TiO@sub 2@) surface has received considerable attention because TiO@sub 2@ is the material of photocatalyst such as the photodecomposition of water. Over the past few years a considerable number of studies have been made on the analysis of rutile TiO@sub 2@(110) surface composition and structure. Most of these studies were conducted using microscopic techniques such as scanning tunneling microscopy (STM) and atomic force microscopy (AFM). However, the information of hydrogen atoms adsorbed on TiO@sub 2@(110) surface seems to be lacking because it is difficult to detect the surface hydrogen using STM or AFM. In the present study, we have investigated the structure and composition of the rutile TiO@sub 2@(110) using coaxial impact collision ion scattering spectroscopy (CAICISS), time-of-flight elastic recoil detection analysis (TOF-ERDA) and low energy electron diffraction (LEED). CAICISS and TOF-ERDA have been proved to be useful techniques for in situ observation of surface structure and composition, in particular, for the determination of the amount of surface hydrogen atoms. When the sample was introduced into ultra high vacuum (UHV) chamber without any treatments, a large quantity of hydrogen and oxygen atoms adsorb on the surface. These atoms can be attributed to water molecules. After annealing the sample at 800°C in UHV, the clean surface of TiO@sub 2@(110) with the LEED pattern of a sharp 1x1 spots was obtained. It was found from the CAICISS measurement that this surface formed bulk terminated structure, known as bridging oxygen rows model. However, it was also found from the TOF-ERDA measurement that the hydrogen atoms still resided on the surface. These hydrogen atoms are not components of water molecules but directly chemisorb on the TiO@sub 2@(110)1x1 surface. Thus, native hydrogen adatoms on the TiO@sub 2@ surface was directly observed and evidenced. Detailed results will be discussed in the presentation.

4:40pm **SS1+MC-ThA9 Work Function Changes and Surface Chemistry of Oxygen and Hydrogen on Indium Tin Oxide**, ***J.A. Chaney***, *P.E. Pehrsson,* Naval Research Laboratory

Indium tin oxide (ITO) is used as a transparent, semiconducting substrate for many device applications. However, there is an inadequate understanding of ITO surface properties, its interaction with gaseous species, and the physical/electronic changes imposed by its surface chemistry. The surface physics and chemistry of oxygen plasma treated ITO were investigated under ultra high vacuum conditions. The work function (@PHI@) of ITO was determined by a vibrating Kelvin probe calibrated with a graphite standard. Sample composition, electronic structure and chemistry were examined by Auger electron spectroscopy (AES), energy loss spectroscopy (ELS), and high resolution electron energy loss spectroscopy (HREELS). Commercial ITO films were heated in-vacuo to remove physisorbed species and then exposed in-situ to oxygen or deuterium activated with a hot metal filament. Oxidation increased the work function from 5.2 to 5.6 eV, but @PHI@ then decayed to <5.2 eV, possibly due to oxygen diffusion into the bulk along defects and grain boundaries. The AES oxygen level was stable after oxidation, and the ELS spectrum consistently showed a strong feature at 0.7 eV for oxidized samples. Deuteration visibly metallized the film and sharply reduced the surface oxygen level. The ELS feature simultaneously disappeared, and the work function decreased to 4.6 eV. The HREELS of clean ITO revealed substantial C-H contamination, which persisted after heating to ~300°C. Even substantial oxygen treatment did not remove the hydrogen signal, suggesting that C-H permeates the ITO film.

5:00pm **SS1+MC-ThA10 Adsorption of Atomic Hydrogen on Both Polar Surfaces of ZnO**, *Th. Becker, M. Kunat, Ch. Boas,* ***U. Burghaus***, *C. Wöll,* Ruhr-University Bochum, Germany

The interaction of atomic hydrogen with Zn-ZnO and O-ZnO surfaces has been investigated by LEED, He atom scattering, He atom reflectivity measurements (as a function of H exposure and surface temperature, T@sub s@), and XPS. Furthermore, measurements of adsorption probabilities of CO on the two polar surfaces of ZnO are presented (see [1] for CO/O-ZnO) as well as the effect of pre-exposed atomic hydrogen on the adsorption dynamics of CO. He atom diffraction measurements indicate the formation of a well ordered H overlayer structure. The strong attenuation of the specular He atom reflectivity by hydrogen exposure indicates, however, a second competing reaction pathway; since extensive exposure to atomic hydrogen leads to a high degree of disorder on the surface. Values for the heat of adsorption for H were estimated from He-atom reflectivity curves, measured as a function of T@sub s@. The shape of the coverage dependent adsorption probability curves, S(@theta@@sub CO@), of CO are for both surfaces consistent with a precursor mediated adsorption; adsorbate assisted adsorption dominates the adsorption. The He atom reflectivity measurements point to the influence of an intrinsic precursor state. A comparison of He atom reflectivity with S(@theta@@sub CO@) curves, respectively, showed that CO initially populates defect sites. The coadsorption of H and CO can be explained by a site blocking mechanism; leading to an estimate of @theta@@sub H@. [1] Th. Becker, Ch. Boas, U. Burghaus, Ch. Wöll, Phys. Rev. B 61(7) (2000) 4538.

Surface Science
Room 209 - Session SS2+NS-ThA
Tribology and Adhesion

Moderator: J. Krim, North Carolina State University

2:00pm **SS2+NS-ThA1 Friction at High Speeds@footnote 1@**, ***J.E. Hammerberg***, *T.C. Germann, B.L. Holian, P.S. Lomdahl,* Los Alamos National Laboratory **INVITED**

The mechanisms of dissipation at dry sliding metal-metal interfaces are complex, nonlinear, and involve a range of length and time scales. Depending upon the magnitude of the relative sliding velocity and the material pressure, phenomena described by phonons, dislocation generation and dynamics, microstructure formation, and mechanical mixing of materials are important. We discuss the variety of these phenomena as seen in extensive very large-scale molecular dynamics simulations for copper and Lennard-Jones systems in two and three dimensions. These simulations suggest universal behavior at large sliding speeds and we discuss some of the theoretical descriptions of these phenomena and recent high speed experimental results. @FootnoteText@ @footnote 1@Work performed under auspices of U.S. DOE at LANL under contract W-7405-Eng-36.

2:40pm **SS2+NS-ThA3 Energy Dissipation Thresholds During Interfacial Shear**, ***N.D. Shinn***, *R.W. Cernosek, S.J. Martin,* Sandia National Laboratories

By measuring the power spectra of clean and surface-modified quartz crystal microbalance resonators in contact with nanometer thick fluid layers, we can detect and quantify energetic thresholds for interfacial slip and other dissipation mechanisms at interfaces under dynamic shear. Understanding fundamental dissipation mechanisms is a necessary prerequisite to mitigating friction via interfacial lubricants or surface coatings. Using an amplified network analyzer, we vary the QCM peak-to-peak potentials, and hence the shear acceleration, over a wide range (0.002-30V) and detect any resultant changes in resonant frequency or resonance damping. This approach allows us to access shear forces otherwise unavailable using traditional QCM oscillator circuits [1] or standard network analyzer systems and therefore to probe stronger interfacial adhesive forces. Initial experiments for water adsorption on polycrystalline Au(111) electrode surfaces with and without a hydrophobic (methyl-terminated) alkanethiol self-assembled monolayer reveal no new dissipation thresholds. This suggests that interfacial slip is not occurring because the nanometer-scale surface roughness is sufficient to entrain the water layer or the energetic barrier for lateral motion remains insurmountable. Experiments are in progress to distinguish interfacial slip thresholds from mechanical entrapment effects by preparing atomically flat microcrystalline domains, contrasting polar and non-polar fluids, and modifying the electrode surfaces with other functionalized monolayers. Research supported by DOE-BES Materials Sciences. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract DE-AC04-94AL85000. @FootnoteText@ @footnote 1@J. Krim and A. Widom, Phys. Rev. B38, 12184 (1988).

3:00pm **SS2+NS-ThA4 Chemical and Mechanical Contributions to the Friction In Self-Assembled Monolayers on Au Surfaces**, ***H.I. Kim***, *J.E. Houston,* Sandia National Laboratories

By studying various combinations of chemically distinct end groups on alkanethiol molecules self-assembled on Au probe/substrate surfaces, and by varying the odd-even length of the chains, we are able to delineate the contributions of chemical and mechani cal effects to interfacial friction. Because it is stable and quantitative throughout the entire range of the interfacial interactions (including the attractive load regime), we use the interfacial force microscope (IFM) to measure the friction force as a function of applied load. For even-length molecular chains, the friction forces progressively increase in the order CH3-CH3, CH3-COOH, COOH-COOH, while the interfacial adhesive force remains virtually identical. In contrast, for odd chain lengths, fricti on and adhesion are low for both CH3-CH3 and CH3-COOH combinations, but much higher for COOH-COOH. By systematically correlating the interfacial adhesion and friction, we conclude that energy dissipation giving rise to sliding friction has distinct chemic al and mechanical components. The making and breaking of hydrogen bonds, due to either intra- or inter-film interactions, gives rise to the "chemical" dissipation while simply disturbing the structure of the film under interfacial sliding invokes the "mechanical" component. This work was supported by the US Department of Energy under Contract DE-AC04-94AL85000. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed-Martin Company, for the US Department of Energy.

3:20pm **SS2+NS-ThA5 Atomic and Molecular Level Insight into Discreet Frictional Events**, ***S.S. Perry***, *T.R. Lee, S.H. Lee, K.I. Kim, R. Colorado, P. Cao, Y.S. Shon, M. Graupe,* University of Houston **INVITED**

Technological advances in a number of industries has driven the need to understand interfacial friction on an atomic and molecular level. This level of understanding requires the careful design of model interfaces and experimental approaches sensitive to atomic and molecular scale events. This has been achieved in our studies by combining two recently developed techniques that operate at the subnanometer scale: control of the interfacial composition through molecular self-assembly or chemical modification under controlled UHV conditions and tribological measurements performed with the atomic force microscope. With this approach, we are able to control or measure the specific chemical composition and structure of interfaces and to correlate changes in composition and structure to the frictional properties of a single asperity contact. Examples will be drawn from both molecularly-thin organic film systems and composite coating systems to illustrate the origins of interfacial friction in terms of the composition and structure of the interface.

4:00pm **SS2+NS-ThA7 Molecular Tribology of Highly Ordered Monolayers***, D. Gourdon,* University of California, Santa Barbara*; C. Duschl,* Swiss Federal Institute of Technology*; **N.A. Burnham**,* Worcester Polytechnic Institute

In order to investigate friction at a fundamental level, atomic force microscopy (AFM) in the wearless regime was performed on a model system - a highly ordered thiolipid monolayer on mica. In the monolayer, condensed domains with long-range orientational order were present. These domains revealed strong friction anisotropies as well as non-negligible asymmetries in the quasistatic friction loops. The directionality of these two effects appeared to correlate well with the tilt direction of the molecules (more specifically of their terminal alkyl chains) in the monolayer. The friction was measured as a function of applied load. The measurements versus load revealed two or three different frictional regimes (depending on the load range), that correlated well with a systematic stepwise behavior of the height of the domain as measured simultaneously. These discrete effects were attributed to molecular gauche defects created under the stress applied by the tip. Other studies include the friction as a function of sliding velocity, chemical preparation of the tip, alternative molecules, and nature of the substrate. Our work suggests that friction on this system is primarily a mechanical phenomenon.

4:20pm **SS2+NS-ThA8 The Effect of C60 on Interfacial Friction and Wetting of Toluene***, **T.S. Coffey**, M. Abdelmaksoud, J. Krim,* North Carolina State University

Experimental investigations of friction, lubrication, and adhesion at nanometer length scales have traditionally been performed using atomic force microscopy (AFM), surface forces apparatus (SFA), or quartz crystal microbalance (QCM) techniques. While collectively these techniques yielded useful information, their results have never been cross-referenced. In order to achieve a cross referencing, we investigated the sliding friction of C60 using AFM, QCM, and macroscopic contact angle measurements. (Recent studies@footnote 1@ suggest that a larger contact angle implies a more slippery interface.) C60 has been previously studied by S.E. Campbell et al. with SFA,@footnote 2@ whereby it was reported that C60 at a toluene/mica interface resulted in a full-slip boundary condition, and C60 was recommended as a possible lubricant. Our contact angle measurements reveal that the contact angle of C60/toluene solutions on mica is greater than the contact angle of toluene alone and therefore support Campbell's result. Using QCM, we have also studied the system toluene/Ag(111) with and without C60 deposited on the silver. These studies indicate that toluene on the C60/silver surface is less slippery than the toluene on the silver alone, and that the contact angle for toluene on C60/silver surface is less than the contact angle for the toluene on the silver. This indicates that C60 is not a good lubricant for a silver surface. We believe that this seeming contradiction with Campbell's result is due to the manner in which the C60 is bound to the mica surface vs. the silver surface. We complete our cross referencing of C60/toluene solutions on these substrates by employing AFM. @footnote 3@ @FootnoteText@ @footnote 1@ J.L. Barrat and L. Bocquet, Physical Review Letters, vol. 82, p. 4671 (1999). @footnote 2@ S.E. Campbell, G. Luengo, V.I. Srdanov, F. Wudl, and J.I. Israelachvili, Nature, vol. 382, p. 520 (1996). @footnote 3@ This work is supported by NSF, AFOSR, and a GAANN fellowship.

4:40pm **SS2+NS-ThA9 Mechanical Behaviour of Confined Films: An In-situ Study of Silane Monolayers by Second Harmonic Generation (SHG)***, **M.T. Strobel**, J. Blümmel, W. Eck, M. Buck, M. Grunze,* University of Heidelberg, Germany

Understanding the tribological properties of ultrathin organic films is of vital interest for their application in micro electro-mechanical systems (MEMS). To elucidate structural aspects of layers confined between two solids SHG was applied to trace force-induced changes of the polar and azimuthal orientation of molecular entities. As a model system monolayers of a silane bearing an SHG-active moiety were adsorbed on a glass-substrate. Mechanical loading and shearing of the film was achieved by a lens pressing against or rolling over the substrate. Mapping the contact area reveals pronounced, site dependent changes of both the tilt angle and the azimuthal alignment of the SHG active moiety upon loading. Whereas the azimuthal alignment persists after unloading and can be controlled by the rolling direction of the lens, the tilt angle is largely reversible for a loading unloading cycle. A quantitative evaluation of the data shows that the degree of the aligment is significantly larger than expected from simple models of contact mechanics.

5:00pm **SS2+NS-ThA10 New Aspects of Friction Force Microscopy in Ultra-high Vacuum***, **R. Bennewitz**, E. Gnecco, T. Gyalog, O. Pfeiffer, Ch. Loppacher, M. Guggisberg, E. Meyer,* University of Basel, Switzerland

Recent experimental results of Friction Force Microscopy in ultra-high vacuum on well defined surfaces give new insight into the atomic processes of friction. On Cu(111), atomic stick-slip behaviour was found for the first time on a metal surface. Lateral stiffness of the contact and its I(V)-characteristic indicate that a copper neck between tip and sample is dragged over the surface.@footnote 1@ The velocity dependence of atomic stick-slip processes was studied on Cu(111) and on NaCl(100) revealing a logarithmic increase of the friction with increasing scan velocity.@footnote 2@ This dependence can be explained by introducing the effects of thermal activation into the Tomlinson model for atomic friction. A new experimental approach to study dissipation processes on atomic scale is the measurement of the damping of vertical and horizontal tip oscillations in the non-contact mode, where power losses of the order of 100 meV per tip osccilation can be detected. @FootnoteText@ @footnote 1@ R. Bennewitz et al., Phys. Rev. B60 (1999) R11301 @footnote 2@ E. Gnecco et al., Phys. Rev. Lett. 84 (2000) 1172.

Thin Films
Room 203 - Session TF-ThA
Transparent Optical Coatings

Moderator: J.R. Doyle, Macalester College

2:00pm **TF-ThA1 Criteria for Choosing Transparent Conductors***, **R.G. Gordon**,* Harvard University **INVITED**

Transparent, electrically conductive films (TCOs) have been prepared from a wide variety of materials. These include oxides of tin, indium, zinc and cadmium, nitrides of titanium and chromium, and metals such as silver and gold. The physical properties of these materials are reviewed and compared. A figure of merit for a transparent conductor may be defined as the ratio of the electrical conductivity to the optical absorption coefficient of the film. The materials having the highest figures of merit are fluorine-doped zinc oxide and cadmium stannate. Physical, chemical and thermal durability, etchability, conductivity, plasma wavelength, work function, thickness, deposition temperature, uniformity, toxicity and cost are other factors that may also influence the choice of material for any particular application. The TCO materials are ranked according to each of these factors. The main applications of TCOs will be examined to see how these factors entered into the selection of the materials actually used.

2:40pm **TF-ThA3 Preparation of Transparent Conducting Thin Films using Multicomponent Oxides Composed of ZnO and V@sub 2@O@sub 5@ by Magnetron Sputtering***, **T. Miyata**, S. Suzuki, H. Toda, T. Minami,* Kanazawa Institute of Technology, Japan

Recently, multicomponent oxides consisting of a combination of different binary or ternary compounds have recently attracted much attention as new transparent conducting oxide (TCO) materials. In this paper, we describe the preparation of TCO thin films using new multicomponent oxides of the ZnO-V@sub 2@O@sub 5@ system. Films were prepared on substrates at temperatures ranging from room temperature (RT) to 350@super o@C by conventional planar magnetron sputtering using powder mixtures of ZnO and V@sub 2@O@sub 5@ as the target. The carrier concentration of vanadium-doped ZnO (ZnO:V) films prepared using ZnOV@sub 2@O@sub 5@ targets markedly increased as the V@sub 2@O@sub 5@ content was increased from 0 to about 15 wt.%, whereas the Hall mobility decreased gradually. As a result, the resistivity of ZnO:V thin films reached a minimum at a V@sub 2@O@sub 5@ content of about 15 wt.%, and markedly increased with V@sub 2@O@sub 5@ contents above about 20 wt.%. Films prepared with V@sub 2@O@sub 5@ contents of about 50 to 70 wt.% were highly resistive or insulators and identified as a ternary compound, ZnV@sub 2@O@sub 4@. In contrast, the resistivity of films markedly decreased as the V@sub 2@O@sub 5@ content was increased from about 80 to 100 wt.%. A 100 wt.% vanadium oxide film with a thickness of 25 nm exhibited a resistivity of 5-10@super -4@@ohm@cm and an average transmittance above 70% in the visible range. In addition, this report describes the chemical properties and the impurity doping effect of TCO films using new multicomponent oxides of the ZnO- V@sub 2@O@sub 5@ system.

3:00pm **TF-ThA4 Properties of Transparent conducting CdO-In@sub 2@O@sub 3@-SnO@sub 2@ Thin Films Prepared by Pulse Laser Deposition (PLD)***, M. Yan, R.P.H. Chang, T.O. Mason, T.J. Marks, K.R. Poeppelmeier,* Northwestern University

Transparent conducting oxides (TCO) have extensive application in display devices, solar cells and sensing elements Various techniques have been applied to deposit TCO films including: thermal evaporation, sputtering, reactive ion plating, chemical vapor deposition (CVD), pulse laser deposition (PLD), atomic layer epitaxy (ALE), etc. The ternary alloy system of CdO-In@sub 2@O@sub 3@-SnO@sub 2@ has received much attention recently. Several compounds in this ternary systems, Cd@sub 2@SnO@sub 4@, CdIn@sub 2@O@sub 4@ and In@sub 4@Sn@sub 3@O@sub 12@, exhibit encouraging electrical and optical properties, while most of the ternary phase diagram (CdO, In@sub 2@O@sub 3@, SnO@sub 2@) remains unexplored. Furthermore, it is believed that there are some metastable phases and solution ranges not available in the bulk form but can be obtained as thin films. In our research, we synthesized and examined the electrical, optical and structural properties of thin films on Si and Corning 1737 substrates with different compositions deposited in a multi-target PLD system. Films were formed by first creating multi-layers of elemental oxides of CdO, In@sub 2@O@sub 3@ and SnO@sub 2@. The stoichiometry of the complex oxide was adjusted during this process. The multi-layered films were then annealed in certain gas environment for a range of time and temperature to form polycrystalline ternary oxides. Preliminary results show that 5% In@sub 2@O@sub 3@ doped CdO has conductivity of 20,000S and bandgap of 2.75eV. Stoichiometric Cd@sub 2@SnO@sub 4@ has conductivity of 1600S and bandgap of 3.02eV. Stoichiometric CdIn@sub 2@O@sub 4@ has conductivity of 600S and bandgap of 3.05eV. When CdIn@sub 2@O@sub 4@ is doped with 5% SnO@sub 2@, its conductivity raised to 3,300S and its bandgap remains unchanged. It is believed that further improvements can be achieved through proper doping and annealing strategies.

3:20pm **TF-ThA5 Expanding Thermal Plasma Deposition of Natively Textured ZnO for Thin Film Solar Cell Applications***, R. Groenen,* Eindhoven University of Technology, The Netherlands*; J. Loeffler,* Utrecht University, The Netherlands*; J.L. Linden,* TNO-TPD, The Netherlands*; R.E.I. Schropp,* Utrecht University, The Netherlands*; M.C.M. van de Sanden,* Eindhoven University of Technology, The Netherlands

A new approach for low temperature deposition of natively textured ZnO is developed, utilizing an expanding thermal argon plasma created with a cascaded arc. (Co)precursors are oxygen, diethylzinc and -additionally for doped films- trimethylaluminum, which undergo ionisation via charge exchange and consecutive dissociative recombination by respectively argon ions and electrons created in the arc. Films are deposited on Corning 1737 F glass at substrate temperatures of 200 - 350°C at a rate of 0.65 - 0.75 nm s@super -1@. The optical and electrical properties relevant for solar cell applications are comparable to those obtained for Asahi U-type SnO@sub 2@:F. Measurements of haze and angular resolved scattering intensity reveal increased light scattering with increasing deposition temperature and film thickness because of a rougher surface texture as confirmed by AFM and SEM measurements. In addition, virtually no loss in transmission of the ZnO films due to hydrogen plasma exposure is observed. In order to demonstrate the suitability for solar cell applications, p-i-n a-Si:H solar cells were co-deposited both on the natively textured low temperature material and Asahi U-type SnO@sub 2@:F, showing comparable efficiencies around 10%. The TCO / p-layer interface leads to effective light scattering, which results in high spectral response especially for long wavelengths.

3:40pm **TF-ThA6 Effects of Excess Oxygen Introduced during Sputter Deposition and Post Annealing under a High Oxygen Pressure on Carrier Mobility in Indium-tin Oxide Films***, N. Kikuchi, E. Kusano, E. Kishio, A. Kinbara, H. Nanto,* Kanazawa Institute of Technology, Japan

Post-annealing for tin dope indium oxide films deposited at a low substrate temperature is sometimes needed to improve their optical properties. While the transparency in the visible range is enhanced by the annealing, the electrical conductivity of the film is deteriorated generally. The deterioration in the electrical conductivity is not only because of the reduction in carrier density, but also because of the reduction in carrier mobility. The reduction in the carrier mobility is thought to strongly relate to the introduction of excess oxygen into or on the film by the annealing. In this paper, indium tin oxide films with excess oxygen was prepared by deposition with a high oxygen concentration or by post-annealing under a high oxygen pressure in order to discuss its effects on electron mobility have been investigated. ITO films were deposited on glass substrates by r.f. sputtering under various oxygen concentrations in the discharge gas (0.3-100 %). Substrate temperature was kept at 773 K during deposition. Single phase of In@sub 2@O@sub 3@ was observed for all films deposited. A minimum resistivity of 1.8x10@super -4@ @ohm@cm was obtained for a film with a Sn concentration of 8 wt%, deposited at an O@sub 2@ concentration in the discharge gas of 0.3 %. With increasing oxygen concentration in the discharge gas from 0.3 % to 100 %, the Hall mobility decreased from 45 cm@super 2@V@super -1@s@super -1@ to 27 cm@super 2@V@super 1@s@super -1@ and the carrier density decreased from 1.0x10@super 21@ cm@super -3@ to 1.0x10@super 19@ cm@super -3@. By the post-annealing at 473 K for 30 min. in air, the Hall mobility of 27 cm@super 2@V@super -1@s@super -1@ increased to 37 cm@super 2@V@super -1@s@super -1@ and the carrier density of 1.0x10@super 19@ cm@super -3@ increased to 2.0x10@super 19@ cm@super -3@. The similar behavior of the Hall mobility and carrier density was observed for an ITO film annealed in O@sub 3@. These increases in the Hall mobility and carrier density during a low temperature annealing is thought to relate to desorption of excess oxygen existed at grain boundaries or the surface of the films because the annealing temperature is too low to improve the film crystallinity further and because it is hard to assume the formation of oxygen vacancies under the condition of the annealing. The results obtained support the hypothesis that the oxygen introduced into grain boundaries or adsorbed at the surface of the films act as charge traps and carrier scattering centers.

4:00pm **TF-ThA7 Preparation and Properties of Transparent Conductive Aluminum-doped Zinc Oxide Thin Films by Sol-Gel Process***, M. Alam, D. Cameron,* Dublin City University, Ireland

Recently, numerous electrically conductive oxides have been discovered and extensively investigated. Of these, indium tin oxide (ITO) and ZnO are well known for their transparency when made into thin films and are expected to find wide use as transparent electrodes for many devices, such as Electrochromic (ECDs), Liquid crystal displays (ELs) and solar cells. Zinc oxide is one of the most promising transparent conducting oxides currently under investigation. Zinc oxide holds considerable promise as an optically transparent conducting material due to its wide band gap (~3.3 eV), its amenability to defect or impurity doping and other desirable properties such as low cost and non-toxicity. Thin films of transparent conducting zinc oxide have been prepared by a variety of techniques, such as sputtering, chemical vapor deposition, reactive evaporation, spray pyrolysis and more recently by sol-gel process. Amongst the different techniques available, the sol-gel method seems to be the most attractive one due to coating on the desired shape and area, easy control of the doping level, solution concentration and homogeneity without using expensive and complicated equipment when compared to other methods. Highly conductive and transparent aluminum-doped zinc oxide thin films have been prepared from the solution of zinc acetate and aluminum chloride in ethanol by sol-gel process. The effect of changing the aluminum-to-zinc ratio from 0 to 6 at. % and annealing temperature from 0 to 600°C in vacuum has been thoroughly investigated. As-deposited films have high resistivity and high optical transmission. Annealing of the as-deposited films in vacuum leads to a substantial reduction in resistivity without affecting the optical transmission. The films have a minimum value of resistivity of about 1.5x10@super-3@ ohm-cm for 0.8 at. % aluminum-doped zinc oxide and a visible transmission of about 90%.

4:20pm **TF-ThA8 Synthesis and Characterization of TCO Cobalt-Nickel Spinel Films***, C.F. Windisch, Jr., K. Ferris, G.J. Exarhos,* Pacific Northwest National Laboratory

Cobalt-nickel oxide films of nominal 100 nm thickness, and resistivities on the order of 0.01 ohm-cm have been prepared by spin-casting from both aqueous and organic precursor solutions followed by annealing at 450 C in air. Films deposited on sapphire substrates exhibit a refractive index of about 1.7 and are relatively transparent in the wavelength region from 600 to 8000 nm. They are also magnetic. The electrical and spectroscopic properties of the oxides have been studied as a function of Co/Ni ratio. An increase in film resistivity was found upon substitution of other cations (Zn@super 2+@, Al@super 3+@) for Ni in the spinel structure. However, some improvement in the mechanical properties of the films resulted. Conducting films also have been prepared upon substitution of cobalt by palladium. A combination of XRD, XPS, UV/Vis and Raman spectroscopy indicated that NiCo@sub 2@O@sub 4@ is the primary conducting component and that the conductivity is maximum at this stoichiometry. When Co/Ni < 2, NiO forms leading to an increase in resistivity; when Co/Ni > 2, the oxide was all spinel but the increased Co content lowered the conductivity. The influence of cation charge state and site occupancy in the spinel structure markedly affects calculated electron band structures and likely influences an anomalous switch of p-type conductivity to n-type conductivity seen at a Co/Ni ratio of 2. Electronic structure modeling studies also suggest the important role of the Ni@super +3@ cation in the conductivity mechanism. Finally, Raman spectra of the films were relatively easy to obtain and therefore were useful as a routine tool for identifying composition and optimizing conductivity.

4:40pm **TF-ThA9 Effect of Vacuum Deposited Polymer Substrate Roughness on ITO Electrical and Optical Properties***, **M.A. Roehrig**, C.I. Bright,* Presstek, Inc.

Increasing interest in next generation flexible flat panel display (FPD) materials and substrates has spurred research into improved/optimized ITO thin films deposited on polymer substrates. Requirements for FPD on flexible substrate are such that high conductivity and optical transmittance must be achieved for very thin ITO thin films, e.g. d@sub ITO@ - 5 nm to 100nm. At these thicknesses, polymer substrate roughness is expected to effect optical and electrical performance of the deposited ITO films making it difficult to achieve the high quality FPD requirements. An organic material vacuum deposition technique with the ability to control polymer film thickness from a few 10's of nanometers to several microns has been combined with ITO deposition from both ceramic (90% In@sub 2@O@sub 3@/ 10% SnO@sub 2@) and metal (90% In/ 10% Sn) targets. The effects of vacuum deposited polymer layer thickness and surface roughness effects on the electrical and optical properties of ITO thin films have been measured. Visible range optical performance, surface profilometry and electrical conductivity measurements, including carrier concentrations and mobilities, have been correlated with the vacuum deposited polymer layer thickness and surface roughness measurements.

5:00pm **TF-ThA10 Properties of Sol-Gel Prepared (ZnO)@sub y@(CdO)@sub 1-y@ Thin Films, with Low Concentrations of Cd in Solution***, C.I. Zúñiga-Romero, **G. Torres-Delgado**, L. Licea-Jiménez, S. Jiménez-Sandoval, O. Jiménez-Sandoval, R. Castanedo-Pérez,* Unidad Querétaro, Mexico

(ZnO)@sub y@(CdO)@sub 1-y@ thin films were prepared by the sol-gel method, with low atomic concentrations (x) of Cd in solution, i.e. 0@<=@x@<=@0.32, at @Delta@x = 0.04 intervals. The precursor solution was mainly based on zinc acetate dihydrate, cadmium acetate dihydrate, and ethylene glycol. The films were deposited on slide glass substrates, and annealed at 400°C, in open atmosphere for 60 min. The X-ray diffraction data show that the films are formed by a polycrystalline mixture of wurtzite-type ZnO and cubic-type CdO; the patterns, as well as electron dispersion spectroscopy (EDS) data, are indicative of a larger concentration (y) of CdO in the films, i.e. 0@<=@y@<=@0.7, with respect to that in solution. In support, the resistivity of the films decreases from @rho@=10@super 2@@ohm@cm for x = 0 (y = 0), to @rho@=5 x 10@super -2@@ohm@cm for x = 0.32 (y = 0.7). The UV-Vis spectra show that the films, throughout the composition range, display a high transmission, above 90%, at @lambda@@>=@600 nm.

Vacuum Technology
Room 201 - Session VT-ThA

Pressure and Flow Measurements

Moderator: N. Peacock, HPS Division, MKS Instruments

2:00pm **VT-ThA1 A Practical Guide to the use of Bayard-Alpert Ionization Gauges***, **J.H. Singleton,*** Consultant **INVITED**

The Bayard Alpert (BA) ionization gauge is the most common device used for the measurement of pressure in vacuum systems. There are however many potential problems in the use of the gauge and in the interpretation of the data that it provides. Perhaps the most basic problem is that the sensitivity of the gauge is substantially different for the common gases encountered in a vacuum system, including hydrogen, argon and nitrogen: if the gas composition is unknown, the absolute pressure cannot be determined. Nevertheless, in many systems, where the gas composition remains constant from day to day, the reading from a BA gauge can serve as a meaningful indicator of relative pressure. But if something goes wrong in the system, such as a water leak, the gauge alone can provide virtually no information as to the problem. This paper is primarily directed to the many other problems that can afflict a gauge; it is an attempt to give practical guidance on the use of a gauge, such as the appropriate connection to a system, and the operating techniques which can be used in order to obtain meaningful data. The topics addressed include gas pumping, by generation of ions, and by chemical interactions at the gauge filament; the change in gas composition by interaction at the gauge filament, and errors in pressure measurement including Barkhausen-Kurtz oscillations, electron stimulated desorption, and the x-ray effect. Factors which dictate the specific BA gauge selection, such as the method used for outgas, and the selection of the electron emitter, will also be discussed.

2:40pm **VT-ThA3 The Ultimate Resolution of Commercial Spinning Rotor Gauges***, **J. Setina,*** Institute of Metals and Technology, Slovenia

The resolution of a spinning rotor gauge (SRG) depends primarily on the precision of measurement of the rotor deceleration rate and on the stability of the rotor residual drag. The ultimate resolution of the SRG can be achieved only when the ambient conditions allow stable residual drag. Our measurements of the residual drag were done in a sealed vacuum system with glass and stainless steel SRG thimbles and a small appendage ion pump. The system was placed in a thermostat together with the SRG suspension head. The suspension head was fixed to the laboratory wall virtually vibration free. The imprecision of the deceleration rate measurements is determined by the rotor frequency and the integration time. Old versions of SRG controllers were limited to the integration time of 30 seconds and the rotor operation frequency was preset to the narrow window of 405 to 415 Hz. Some new versions of controllers allow the extension of the integration time to 60 seconds and the operation of the rotor at frequencies up to 800 Hz. In the present study we varied the integration time and rotor frequency and observed the statistical distributions of sequential readings of the rotor residual drag. We found some instabilities of the gauge immediately after the re-acceleration of the rotor. Such instabilities were not reported previously and can affect the accuracy of pressure measurements. We also found that operation of the rotor at higher speeds increases the frequency dependence of the residual drag.

3:00pm **VT-ThA4 Extending the Upper Pressure Limits of Cold-Cathode Gauges***, **B.R.F. Kendall,*** Elvac Laboratories*; E. Drubetsky,* Televac Division of the Fredericks Company

Processes occurring in magnetron-type discharges at normal and elevated pressures are compared. As pressures rise into the micron range, an increasing fraction of electron-molecule interactions occur at less than ionizing energies, and more of the ions collide with molecules on their way to the cathode. This results in fundamental changes in the discharge behavior. Discharge currents have been measured as a function of pressure and voltage up to 1 Torr for a number of magnetron and inverted magnetron electrode configurations. Additional experiments covered AC and pulsed operation. Practical aspects of high-pressure operation such as sputtering, electrode heating and the formation of polymer films are reviewed. The possibility of operating a double inverted magnetron at pressures approaching 1 Torr is discussed. Simple extended-range gauges of this type could replace complicated hybrid gauge combinations in some applications.

3:20pm **VT-ThA5 An Absolute Vacuum Gage Based on the Q Value of the Vibration of a Silicon Micro Cantilever***, **Y. Kawamura,*** Fukuoka Institute of Technology, Japan

The Q value of a silicon micro cantilever has been measured in vacuum under the condition of ultra micro amplitude of the vibration. The maximum Q value of about 30000 was obtained in the vacuum of 1x10-6 torr. The measured Q value was in good agreement with the theoretical calculations based on the momentum exchanges between the cantilever and gas molecules. This system can be expected to be applied to a new type of absolute vacuum gage.

3:40pm **VT-ThA6 Performance of the Axial-symmetric Transmission Gauge Improved for the Measurement of Wide Pressure Range***, **H. Akimichi**, N. Takahashi, T. Hayashi, Y. Tuzi,* ULVAC Japan, Ltd., Japan

The axial-symmetric transmission gauge (AT gauge) is originally developed for the pressure measurement in extreme high vacuum . The Bessel-Box type energy analyzer is placed between the ionizer and the ion collector with a secondary electron multiplier (SEM). The analyzer prevents the SEM from the effects of soft x-rays and electron stimulated desorption (ESD) ions produced in the ionizer. The lower limit of the pressure measurement was estimated to be about 10 @super -12@ Pa. The higher limit, however, was restricted to about 10 @super -6@ Pa due to the limit of pulse resolution of the SEM. In order to expand the pressure measurement up to high vacuum range (~ 10 @super -2@ Pa), the SEM was replaced by a Faraday cup type ion collector. The sensitivity factors of the gauge calibrated by the Conductance Modulation Method through the pressure range of 10 @super -10@ to 10 @super -6@ Pa were (6.7 ± 0.2) x 10 @super -3@ Pa @super -1@ for nitrogen and (2.3 ± 0.04) x 10 @super -3@ Pa @super -1@ for hydrogen, respectively. Comparison of the AT gauge to the extractor gauge (EG) and the spinning rotor gauge also gave the sensitivity factor of (5.8 ± 0.1) x 10 @super -3@ Pa @super -1@ for nitrogen in the pressure range of 10 @super -8@ to 10 @super -2@ Pa. When oxygen was introduced into the system with an AT gauge and a conventional EG, the nominal pressure readings of the EG showed higher values than those of the AT gauge. The difference increased with the increment of oxygen pressure and exposure, and decreased to zero by the bake-out of the system during the pumping process. The results show that the ESD ions, originated from the oxygen adsorbed on the grid surface of ionizer, are effectively separated from the gas phase ions by the energy analyzer in AT gauge.

4:00pm **VT-ThA7 Study of Thermal Transpiration of Capacitance Diaphragm Gauge by DSMC Method***, **M. Hirata**, S. Nishizawa,* Electrotechnical Laboratory, Japan*; K. Watanabe,* CRC Corporation, Japan

Capacitance diaphragm gauge (CDG) is one of the most important vacuum gauges in low and middle vacuum ranges. Sensor head of a high precision CDG is kept for 45°C in order to minimize zero drift from room temperature fluctuation. The difference of temperature between the sensor head and the vacuum chamber gives a non-linear sensitivity of the gauge depending on the pressure less than 130 Pa due to thermal transpiration effect. Change in the sensitivity of about 4 % between molecular flow regime and viscous flow regime is significant for metrological use of the gauge. Empirical equation is widely used to explain the effect.@footnote 1@ In this study, by using a direct simulation Monte Carlo (DSMC) method @footnote 2@, pressure distribution in the connecting tube of the gauge was obtained under the pressure range from molecular flow regime to viscous flow regime (10@super -2@ - 10@super 2@ Pa) with taking account of temperature distribution along the connecting tube. Furthermore, the pressure dependence of sensitivity of CDG for several gases was derived from the pressure difference between the hot and cold ends. It was in good agreement with the pressure dependence of sensitivity obtained by static expansion system experimentally. The pressure distribution inside the connecting tube explains the mechanism of thermal transpiration phenomenon. This method can be also applied for complicated real system. @FootnoteText@ @footnote 1@ T.Takaishi and Y.Sensui, Trans.Faraday Soc. 59, 2503(1963). @footnote 2@ G.A.Bird, "Molecular Gas Dynamics and the Direct Simulation of Gas Flows", Clarendon, Oxford (1994).

4:20pm **VT-ThA8 Intelligent Flow Measurement and Control***, **G.H. Leggett**, S.A. Tison, K. Tinsley,* Millipore Corporation

Vacuum processes typically use mass flow controllers for delivery of stable and known flow of gas to the process chamber. A variety of techniques are used for gas measurement and control, but the most prevalent is based on thermal transfer between a heated tube wall and the gas stream. This class of mass flow controller is referred to as a thermal mass flow controller. These instruments have been in use for over 20 years and have evolved with time. Most recent versions are digital controllers which allow for digital setpoints and digital outputs. While advances have been made, MFCs are still custom manufactured for a particular gas and flow range, and their accuracies with process gases is typically no better than +/-5%. A new thermal based MFC has been developed which is capable of operating over extended ranges (500 to 1 flow ratios) and is able to achieve accuracies with process gases to within 1% of the MFC full scale. These accuracies are attained by using theoretical and empirical based techniques for relating the flow of the calibration gas to that of the process gas. Similar techniques are used for tuning of the MFC to ensure typical response times of one second. This paper describes the design, control techniques, calibration processes, and verification data for a thermal based mass flow controller with typical semiconductor process gases.

4:40pm **VT-ThA9 Summary of the Extreme High Vacuum and Surface Conditioning Workshop***, **G.R. Myneni**,* Jefferson Lab, US

Summary of the Extreme High Vacuum and Surface Conditioning Workshop The Vacuum Technology Division, the Mid-Atlantic Chapter of the AVS and the Jefferson Lab have sponsored a workshop on Extreme High Vacuum and Surface Conditioning at Jefferson Lab in June 2000. The main focus of the workshop was the limitations of various pumps in achieving XHV. The deliberations included kinetic pumps (turbo-molecular pumps), and capture pumps (ion pumps and cryopumps). Discussions on improvements in vacuum measurement techniques, extreme sensitivity helium leak detection practices, as well as the calibration of such advanced instrumentation systems were an integral part of the workshop. The various topics of interest that were covered in technical sessions include: applications of XHV technologies, a quantitative understanding of virtual leaks, means to eliminate or reduce the various gas sources in XHV systems, XHV materials, XHV vacuum system fabrication methods, XHV technology standards and development of low cost XHV systems. High lights of this workshop will be presented in this talk.

Biomaterial Interfaces
Room 202 - Session BI-FrM

Biomolecular Recognition at Surfaces

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

8:20am **BI-FrM1 AFM and EM Studies Providing Insights into Membrane Fusion in Cells*, B.P. Jena,*** Yale University School of Medicine **INVITED**

Binding force profiles between solubilized synaptic vesicle and synaptosomal membrane components were examined using atomic force microscopy (AFM). These AFM force spectroscopic studies reveal that a 17 nm and a 34 nm long complex form, following interaction between the two sets of membrane components. The formation of such complexes is further confirmed using negative staining electron microscopy (EM), performed on the immunoprecipitated membrane fusion machinery obtained from neuronal tissue. These EM studies performed on the dehydrated immunoprecipitated native fusion complex reveal the presence of 28-30 nm new coiled rod-like structures in association with 14 nm long SNARE complexes. Neuronal SNAREs were found coiled and super-coiled with these structures. The existence of NSF as pentamers in its native state is also demonstrated. The extent of coiling and super-coiling of SNAREs may regulate the potency and efficacy of membrane fusion in cells.

9:00am **BI-FrM3 Adhesion of Mammalian Cells Modeled by Functionalized Vesicles*, A. Janshoff,*** *J. Wegener, H.-J. Galla,* WWU Muenster, Germany

Specific molecular recognition between cell-surface receptors and extracellular matrix proteins immobilized on a growth substrate are the most relevant interactions that allow cells to actively spread on a surface. We applied the quartz crystal microbalance technique (QCM) to follow the time course of cell attachment and spreading on artificial substrates. The shift of the sensorÂ´s resonance frequency provides a direct measure for the fractional surface coverage of the piezoelectrically active area. Frequency shifts associated with the establishment of confluent cell layers were found to be dependent on the cell species, reflecting their individual impact on the displacement of the resonator. In order to learn more about the mechanisms that govern the response of shear wave resonators to the attachment of mammalian cells, we modeled the cellular system with unilamellar liposomes doped with biotinylated lipids. Liposome adhesion to avidin/streptavidin coated surfaces was monitored using the QCM technique. Increasing fractions of the biotinylated lipid in the liposome shell resulted in enhanced shifts of the resonance frequency. Concomitant shape analysis of the surface-attached vesicles using SFM revealed an extended contact area between liposome and surface. We conclude, that an increasing number of bonds between the liposome and the surface induces the extended contact areas and that a similar mechanism may be applicable to explain the individual response of the QCM to different cell species.

9:20am **BI-FrM4 PNA-DNA and DNA-DNA Hybridization Detection via Lipid-Biotin-Streptavidin Immobilization on a SiO2 Coated Quartz Crystal Microbalance Sensor*, F. Höök,*** *A. Ray, B. Norden, B. Kasemo,* Chalmers University of Technology, Sweden

Surface-based bioanalytical sensors for oligonucleotide hybridization are very attractive for genetic diagnostics, gene therapeutics and the emerging solid phase / real time PCR. Little is however known about how various immobilization strategies affect the conformation and hence function of oligonucleotide strands. We have investigated the possibility to use the dissipative quartz crystal microbalance (QCM-D) technique and controlled surface-immobilization of single stranded synthetic peptide nucleic acid (PNA) as well as DNA, as selective probe(s) for fully complementary and various single mismatch DNA. In order to minimize unspecific binding of DNA, streptavidin was immobilized as a protein 2-D crystal on a biotinylated phospholipid bilayer supported on a SiO@sub 2@ surface in the fluid liquid crystalline phase. This was followed by attachment of a mixed-sequence 15-mer biotin-PNA or a 15-mer biotin-DNA with identical base pairs. The exposure of the streptavidin-immobilized biotin-PNA and biotin-DNA to fully complementary and various mismatch DNA was investigated at 24 °C. Only the fully complementary and singly mismatched DNA oligomers hybridized with the immobilized PNA and DNA, and was possible to discriminate via significant difference in the binding and dissociation kinetics, demonstrating a very high selectively. Most interestingly, however, is that the ratio between hybridization-induced energy dissipation (c.f. rigidity) and the frequency shifts (c.f. mass uptake), allowed us to discriminate different structures of immobilized PNA-DNA and DNA-DNA duplexes. Possible influence on the hybridization kinetics and the structure of the formed duplexes from primarily lateral interaction is discussed.

9:40am **BI-FrM5 DNA Probe Structure and Target Length Effects on Hybridization Kinetics and Efficiency of DNA Self-assembled Monolayers*, G.B. Saupe*,** *M.J. Tarlov,* National Institute of Standards and Technology

Optimizing the parameters involved in monolayer DNA hybridization events is important to the emerging DNA sensor array technologies used for a variety of applications including genetic diagnostics, forensics, and infectious disease detection. The objective of our research is to determine how DNA surface coverage, molecular orientation, and sequence identity impact the functionality of DNA array devices. To study these factors we use a model system with short sequences of single-stranded DNA probes self-assembled on gold surfaces through a thiol linker. The gold is also passivated with mercaptohexanol to eliminate non-specific adsorption of DNA to the gold and to enhance the activity of immobilized probes. Surface Plasmon Resonance is used to monitor and derive, in situ, the nanometer-scale thickness changes associated with surface hybridization reactions. Complementary single-stranded DNA targets in high salt buffered solutions hybridize with relatively high efficiency (25-100%) to these surface bound probes. We will report how variations in probe surface structure, the length of ssDNA targets, and the relative position of the complementary sequence in the ssDNA targets affect hybridization kinetics, efficiencies and completion times.

10:00am **BI-FrM6 Probing Protein Interactions with Surface-Immobilized Double-Stranded DNA Using Surface Plasmon Resonance Sensing Techniques*, J.S. Shumaker-Parry,*** *C.T. Campbell, K.E. Nelson,* University of Washington*; G.D. Stormo,* Washington University Medical School*; F.S. Silbaq,* University of Colorado*; R.H. Aebersold,* University of Washington

Understanding the molecular mechanisms of gene expression in eukaryotes requires a precise knowledge of the strength and specificity of protein:DNA interactions. Surface plasmon resonance sensing techniques are important for monitoring the adsorption of biomolecules from liquid solutions onto functionalized solid surfaces with high sensitivity and fast time response. Simple methods convert changes in the angle or wavelength at which the surface plasmon resonance (SPR) of a thin metal film is optically excited into adsorbate concentrations. Methods for monitoring interactions between the transcription repressor protein Mnt and surface-immobilized double-stranded DNA using SPR spectroscopy and microscopy will be described. We have immobilized dsDNAs onto a planar gold surface with high density (1-3x10@super 12@ DNA/cm@super 2@, depending on their length) and uniform spacing (~4 nm closest possible DNA-DNA separation). This was accomplished by adsorbing biotinylated DNAs onto a nearly close-packed monolayer of the protein streptavidin prepared first by adsorbing it onto a mixed self-assembled monolayer on gold containing biotin-terminated and oligo(ethylene glycol)-terminated alkylthiolates in a 3/7 ratio. This DNA-functionalized surface resists non-specific protein adsorption. SPR spectroscopy experiments have shown that Mnt binds in 3.8:1 ratio to its immobilized DNA recognition sequence. This is consistent with its behavior in homogeneous solution, where it binds as a tetramer to its DNA binding sequence. A sequence with a single base-pair mutation shows nearly as much Mnt binding, but a completely random DNA sequence shows only 5% of this binding. This proves that DNA-binding proteins bind sequence-specifically to dsDNAs that are immobilized to gold with this streptavidin linker layer. SPR microscopy is being developed to extend these studies to probe protein interactions with an array of dsDNA-containing elements immobilized on a sensor surface.

10:20am **BI-FrM7 Immobilized Antibodies on Functionalized Self-assembled Monolayers: Reactivity, Surface Homogeneity and Microarraying*, P. Kernen*,** *F. Zaugg, K. Witte, D. Quincy, P. Indermuehle, S. Nock, P. Wagner*, Zyomyx Inc.

@omega@-Substituted alkanethiols self-assemble in ordered monolayers on Au(111) surfaces and form highly reproducible reactive interfaces for biomolecule immobilization. Reaction conditions for covalent coupling of antibodies to monolayers exposing N-hydroxysuccinimide and other functionalities have been tested using radiometry and fluorescence microscopy. Scanning probe microscopy, X-ray photoelectron spectroscopy and other surface analytical techniques have been applied to characterize homogeneity and surface coverage of covalently bound biomolecules. By incorporating these bioreactive interfaces into microfabricated three-dimensional structures in silicon, functional microarrays of antibodies could be produced with variable feature size.

Material Characterization
Room 207 - Session MC+NS-FrM

Characterization of Interfaces and Thin Films

Moderator: L.A. Giannuzzi, University of Central Florida

8:20am **MC+NS-FrM1 RBS, AFM, and AES Characterization of Pt Films Deposited by Ion Assisted CVD***, **B. Rogers**, K.A. Telari, H. Fang, L. Shen, R.A. Weller,* Vanderbilt University*; D. Braski,* Oak Ridge National Laboratory

The semiconductor industry has used focussed ion beam (FIB) systems for several years to create site specific transmission electron microscopy (TEM) and secondary electron microscopy (SEM) cross sections, repair lithography masks, and to reroute electrical current by cutting and creating current carrying paths for circuit testing. The FIB systems' capability to both etch and deposit material in defined areas makes them good candidates for use as flexible processing systems for the development of specialized circuits. For example, metal patterns deposited in a FIB system could be used to form electrical connections and sensors on micro-electromechanical systems (MEMs) devices. Properties of the deposited material as well as the process by which it is deposited must be well characterized in order for the material to be successfully used in this type of development program. This work presents results from characterization of the ion assisted chemical vapor deposition of Pt from trimethyl(methylcyclopentadienyl)platinum [C@sub 9@H@sub 16@Pt]. Films were deposited in squares ranging from 50µm on a side to 400 µm on a side. Process parameters, including precursor temperature, dwell time, and ion beam current were varied to investigate their affect on the composition of the deposited films. A specially designed sample holder and Be mask enabled Rutherford backscattering spectrometry (RBS) determination and comparison of the Pt areal densities in these small features. Atomic force microscopy was used to determine the thickness and surface morphology of the deposited films. Scanning Auger electron microscopy was used to analyze the films for oxygen and carbon. Results show that the films contain a large amount of carbon and gallium in addition to the desired platinum. The presentation will conclude with a discussion of the effects of process parameters on the films' composition and possible pathways to maximize the platinum content of the films.

8:40am **MC+NS-FrM2 Material and Interface Characterization of Locally Deposited Dielectrics and Metals Fabricated with a Focused Ion Beam (FIB)***, **H.D. Wanzenboeck**, H. Langfischer, E. Bertagnolli, H. Stoeri, M. Gritsch, H. Hutter,* Vienna University of Technology, Austria

A chemical vapor deposition process was performed under vacuum conditions utilizing a focused ion beam (FIB) tool confining the deposition on a selected area in the Âµm down to the deep sub-Âµm range. The direct fabrication by FIB offers a versatile approach for rapid development and instant testing of novel microelectronic devices. The electrical properties of devices are influenced by the bulk attributes of the material. For complex multilayer structures the interface between 2 materials is of crucial importance. A focused Ga ion beam with diameter down to 5 nm was applied to induce decomposition of selected metalorganic species and siliconorganic compounds adsorbed on the sample surface. Deposition of metals was achieved by using metalcarbonyls such as W(CO)6 as precursors. Dielectrics such as siliconoxides were deposited by coadsorption of siloxane and pure oxygene. For siliconoxide the mixture ratio of the volatile precursor gases was found to be decisive for the chemical composition and electrical properties. For material characterization multilayer structuresof dielectric and metal have been investigated. Auger-Spectroscopy revealed a correlation between the chemical composition of the FIB-deposited layers their electric characteristics and the process parameters chosen. Images of the X-section of the surface and interface deposited layers showed a homogeneous bulk density and a satisfactory surface roughness. Although the interface between FIB-deposited metal and dielectric layer is clearly visible in the secondary electron image depth profiling by secondary ion mass spectroscopy (SIMS) suggests an altered layer due to atomic mixing by the ion beam in a typical range up to 100 nm. The refined comprehension allowed to optimize the process parameters foraer improved material properties.

9:00am **MC+NS-FrM3 Three-Dimensional Material Characterization using Focused Ion Beams (FIB)***, **R.J. Young**,* FEI Company **INVITED**

The focused ion beam (FIB) system is integral to the manufacture of semiconductor and data storage devices. Systems are now found throughout the manufacturing process, from the research laboratory to the production line. The ability of the FIB to image at high resolution, and to locally sputter and add material, provides capabilities not obtainable with optical and scanning electron microscope (SEM) techniques alone. FIB techniques include cross-sectioning, gas-assisted etching and deposition, circuit editing, ion channeling imaging, secondary ion mass spectroscopy (SIMS), and transmission electron microscope (TEM) thin film preparation. In addition, combining together the FIB and SEM in a single instrument (a "dual beam") produces an extremely powerful and flexible materials characterization system, providing unique three-dimensional subsurface metrology and analysis capabilities. In particular, the electron beam can be used to image the face of the cross section as it is being milled by the ion beam. This greatly aids in the location of very small defect sites. Further, the use of in-situ delineation etching allows the whole process of sample preparation to final imaging to be carried out in a single instrument. It should also be noted that SEM and FIB images and analysis techniques are in many ways complementary, the different contrast mechanism in each case giving additional information about the sample. Many of the FIB and dual beam techniques used in the analysis and sample preparation of microelectronic devices apply equally to other disciplines. In particular, the ability to locate, expose and then analyze submicron or unique defects has a wide applicability within material and biological sciences. This paper reviews the capabilities of focused ion beam systems, illustrating these with a number of case studies.

9:40am **MC+NS-FrM5 Visualizing Interfacial Structure at Non-Common-Atom Heterojunctions with Cross-Sectional Scanning Tunneling Microscopy@footnote 1@***, **J. Steinshnider**, M. Weimer,* Texas A&M University*; R. Kaspi,* Air Force Research Laboratory*; G.W. Turner,* Lincoln Laboratory, M.I.T.

We describe how scanning tunneling microscopy (STM) may be used to image the interfacial bonding across the nearly-lattice-matched, non-common-atom GaSb / InAs heterojunction with atomic-scale precision. An ideal, compositionally-abrupt GaSb / InAs interface introduces new bonds - either InSb-like or GaAs-like - whose natural lengths differ from those in the surrounding host materials. These bond length differences are readily distinguished following (110) cleavage of the heterojunction, which locally relieves the out-of-plane compressive or tensile strain otherwise accommodated by a lattice-mismatched interface. The method is equally applicable to AlSb / InAs and suggests how it might be possible to determine the interfacial structure of such non-common-atom heterojunctions from atomic-resolution STM data.@FootnoteText@@footnote 1@Work supported by the National Science Foundation, Division of Materials Research, and the Air Force Research Laboratory

10:00am **MC+NS-FrM6 Atomic Resolved Spectroscopic Study of AlGaAs/GaAs/InGaAs by Cross-sectional Scanning Tunneling Microscope***, **J. Yu**, L. Liu, J. Li, J.W. Lyding,* University of Illinois

An atomic resolved cross-sectional STM spectroscopic study has been performed on UHV-cleaved AlGaAs/GaAs/InGaAs heterostructures. Current imaging tunneling spectroscopy (CITS) results demonstrate significant electronic structure contrast between the column III and V sublattices as well as for the different compositional regions. The resulting images reveal surface structures not always evident in topographic images. Using a pattern recognition algorithm derived from the VERI analysis developed at Sandia,@footnote 1@ the image pixels can be grouped into classes according to similar electronic structure. This technique can be applied to automatically identify the spatial distribution of various elements during semiconductor growth. A detailed analysis and physical explanation of the spectra will be presented. @FootnoteText@@footnote 1@Bouchard, A. M., Osbourn, G. C., and Swartzentruber, B. S., Surf. Sci. 321, 276 (1994).

10:20am **MC+NS-FrM7 Scanning Spreading Resistance Microscopy of MOCVD Grown InP Structures***, **St.J. Dixon-Warren**, S. Ingrey,* Nortel Networks, Canada

Scanning spreading resistance microscopy (SSRM) is a new probe microscopy technique that provides localized resistance profiling over a semiconductor surface. The technique, which is based on contact-mode atomic force microscopy (AFM), provides information on the two dimensional distribution of charge carriers and on the position of pn junctions in semiconductor structures. We have used SSRM to examine the cleaved edge of a number of MOCVD grown InP structures, including multi-quantum well layers and buried heterojunction laser structures. Information on the spatial distribution of dopants in the InP epitaxial layers was obtained. The effect of the applied tip voltage was investigated. We found that the active region of the laser structure, where the band gap is lowest, could be identified in the voltage dependence of the SSRM images.

The effect of scanning rate, surface preparation and tip choice will also be discussed.

10:40am **MC+NS-FrM8 XPS Analysis of Interfacial WO@sub x@ using Linear Least Squares and Standard Curve Fitting Routines***, **D.K. Fillmore**,* Micron Technology, Inc.

X-ray photoelectron spectroscopy (XPS) has proven itself extremely useful in determining the chemical states of various materials. These chemical state identifications are primarily inferred from characteristic peak shapes and energy shifts along with the correlating presence of other elements and a previous knowledge of typical chemical compounds. When several chemical species are present in a particular sample, standard curve fitting routines are employed to extract the individual spectral components from multi-component spectra. This entails significant care in assigning each of the individual component peak energies, relative intensities and characteristic widths. The problem is exacerbated when ion sputtering is employed which results in sputtering-induced decomposition of components. From the curve-resolved data, atomic concentrations of individual components in a multi-component sample may be obtained. By making certain assumptions in specific circumstances, linear least squares (LLS) analysis routines may be able to quickly extract similar atomic concentration data from multi-component spectra without explicitly identifying individual spectral component peaks. This paper will discuss and compare analyses of interfacial WO@sub x@ found between a surface SiO@sub 2@ layer and underlying elemental W using both LLS and standard curve fitting analysis routines. Specific advantages and disadvantages of each approach will be covered.

11:00am **MC+NS-FrM9 Investigations into the Chemical Nature of the Interfaces of Cu and Ta with SiN***, **J.F. Bernard**, E. Adem, S. Avanzino, M.-V. Ngo,* Advanced Micro Devices

Surface chemistry is typically related to film properties such as adhesion, wetability, etc. For Cu interconnects the surface mobility of of Cu ions can affect electromigration and line-to-line leakage in damascene structures.@footnote 1@ The surface treatment of Cu after CMP planarization will effect the chemical nature of the interface with the capping material as well as the interface of any liners with the cap. The chemical nature of the interface of Cu with SiN has been determined through XPS and AES compositional and chemical state depth profile analyses. The effect of plasma treatments on the Cu surface and resulting interfaces with the SiN capping layer is detailed. A mechanism for the Cu° catalyzed generation of the observed interfacial non-N bonded Si resulting from a silane based SiN deposition is proposed. Additionally, the interface of SiN with Ta is investigated to explore the effects of Cu treatments on the liner/cap interface. The basic outgassing behaviors of Cu and Ta are also discussed relative to the effects observed at the interface with the SiN capping layer. @FootnoteText@ @footnote 1@ Noguchi, J., "TDDB Improvement in Cu Metallization under Bias Stress"; International Relaiabilty Physics Symposium 2000.

11:20am **MC+NS-FrM10 On the Organic Content and Outgassing Behavior of Organometallic-based CVD-TiN Films***, J.F. Bernard, **E. Adem**,* Advanced Micro Devices

The drive to smaller IC geometries has led to an increasing use of organometallic precursor based chemical vapor depositions of TiN barrier films. The CVD-TiN process yields more uniform step coverage in high aspect ratio features. The CVD process also presents challenges in generating a consistently high quality TiN film. At lower temperatures both organometallic and metal halide precursors yield a lower density film with high resistivity and low N conents. A N-based treatment process has been widely employed to i)reduce the organic component and ii)increase the N content of the films resulting from the use of TDMAT or TDEAT organometallics. The remaining C in the film has been shown to be present as a cabide of Ti. The chemical state of this remaining C has been further examined through the use of depth profiling, FT/IR, and wet chemical etching techniques. Deviations in the plasma treatment or the as deposited thickness can have a significant effect on the film quality. The affinity for O exhibited by uncapped PVD-TiN is higher still for untreated CVD films. The evolved gas profiles for a low resistivity film are dominated by H/H@sub2@ outgassings. Films with a deviation in plasma conditions exhibited higher resistivity beyond spec limits and outgassings dominated by OH.

Magnetic Interfaces and Nanostructures
Room 206 - Session MI-FrM

Magnetic Recording: Media and Heads

Moderator: D.K. Weller, IBM Almaden Research Center

8:20am **MI-FrM1 Focused Ion Beam Patterning of Magnetic Films***, **B.D. Terris**, C.T. Rettner, M.E. Best,* IBM Almaden Research Center **INVITED**

In the future it may be necessary to pattern magnetic recording media to achieve data densities beyond 100 Gb/sq. in. The required patterning should have minimal cost and leave a surface suitable for flying a recording head. One promising approach to achieving such patterning is to use ion beams to directly modify the magnetic properties of thin films. It has been shown previously that Co/Pt multilayers can be modified magnetically by exposure to a uniform beam of ions (eg. He+, N+), where the easy magnetization axis of the film is rotated from out-of-plane in the as grown film to in-plane in the irradiated film. Local areas of in-plane magnetization can thus be produced by exposing the film through masks.@footnote 1-3@ We have now demonstrated that such films can be also be patterned using a focused ion beam (FIB) of Ga+ ions without the use of a mask. In addition to patterning the multilayer Co/Pt films by easy axis rotation, films of granular CoPtCr have been patterned by removal of the magnetic film by Ga+ milling. The remanent magnetization state of square islands ranging from 80 nm to 230 nm in size was studied by MFM and the smallest islands appear to be single domain. Remanent hysteresis loops generated from MFM data show that the coercivity of the CoPtCr films is unchanged by the FIB patterning, in contrast to the FIB patterning of Co/Pt multilayers where the coercivity decreases with increasing ion dose and decreasing island size. @FootnoteText@ @footnote 1@C. Chappert et al., Science 280, 1919 (1998) @footnote 2@B. D. Terris et al., Appl. Phys. Lett.75, 403 (1999) @footnote 3@T. Devolder et al., Appl. Phys. Lett. 74, 3383 (1999)

9:00am **MI-FrM3 Interface Reactions between Quaternary Cobalt Alloys and Carbon Overcoats in Thin Film Disk Media***, **J.-U. Thiele**, D.J. Pocker, R.L. White,* IBM Storage Technology Division

In the magnetic disk drive industry's quest for ever higher data storage areal densities, the head-to-disk spacing and consequently the film thicknesses of all functional layers of magnetic media continue to decrease. In the future the thicknesses of magnetic storage layers and carbon overcoat can be expected to approach the typical thicknesses of chemical interface reactions, i.e. thicknesses of the order of a few nanometers. Here we present a core level X-ray photoelectron spectroscopy study of interface reactions between CoPtCrB and CoPtCrTa magnetic alloy layers and 35 Å thick protective hydrogenated and nitrogenated carbon overcoats on metal hard disks. In comparing CoPtCrTa alloy films with a nitrogenated carbon overcoat to the same media with hydrogenated carbon overcoats we find a drop in coercivity of up to 200 Oe. The formation of tantalum nitride as well as small amounts of chromium nitride was detected in the photoelectron spectra. Conversely, spectra of nitrogenated carbon films on B-containing alloys showed the formation of boron nitride and small amounts of chromium nitride at the interface. The amount of boron nitride varies depending on substrate bias voltage and temperature. Surprisingly, no effects of these interface reactions on the magnetic properties of the disks could be detected. In summary, while the formation of boron nitride at the interface of CoPtCrB media and protective carbon overcoat does not affect the magnetic properties of the disks in the range of boron and nitrogen concentrations investigated here, small changes in the chemical environment of Ta and/or Cr can lead to significant changes in the magnetic properties of the CoPtCrTa media.

9:20am **MI-FrM4 Corrosion Behavior of CoSm Based Magnetic Media***, **I. Zana**, G. Zangari,* The University of Alabama

Future state-of-the-art magnetic recording media require high coercivity and magnetization and from a low noise stand point, a small grain size. To achieve these properties, alloys and compounds with high anisotropy are being considered. Among them, we previously reported on rare-earth transition metal CoSm thin films@foontote 1@ with very good magnetic properties. Despite these attractive magnetic properties, the potentially high susceptibility to corrosion, due particularly to the rare-earth element, rises the question of chemical stability for these alloys and therefore on the practicality of CoSm system. In order to investigate the chemical stability of a CoSm system, we fabricated a series of samples on glass substrates, by sputtering. To evaluate the influence of the roughness of both underlayer and magnetic layer, we sputter Cr as underlayer with thickness of 20, 60 and 100 nm. Onto each Cr underlayer, the magnetic layer has a thickness of 8 and 16 nm. These samples were further coated, without breaking the vacuum, with a protective layer of C-N and Si3N4 (2 to 8 nm thickness). A series of samples has been left intentionally unprotected. Corrosion resistance of the samples has been tested by high temperature /humidity accelerated aging and annealing under various atmospheres. Structural and chemical uniformity, roughness as well as stability of the magnetic properties of aged samples have been evaluated by use of x-ray photoelectron spectroscopy, electron microscopy, x-ray diffraction and magnetometry. By comparison with unprotected samples and with commercial disk structure, we found that (a) Si3N4 protective layer strongly improve the corrosion resistance and stability of the magnetic layer and (b) CoSm layers protected by Si3N4 exhibit stability comparable or superior to commercial hard disk. @FootnoteText@@footnote 1@I. Zana, G. Zangari, "Magnetic Interactions and Thermal Stability in CoSm Thin Films", accepted to publication in IEEE Transactions on Magnetics.

9:40am **MI-FrM5 Preparation and Characterization of High-Coercivity Cobalt Ferrite Particles Using Microemulsions***, **H. Du**, Y. Kim, S.L. Lim, L. Si, J. Ding,* National University of Singapore*; W.S. Chin,* National University of Singapore, Singapore

Ferrite materials in nano-scale are potential candidate for application on magnetic recording in high density and the study of nanoscale magnetic domains is of both fundamental and technical interest. In order to get uniform particles in nanosize, we attempted to separate the nucleation and growth processes. The nuclei of precursor hydroxides were formed in reverse micelles of sodium dioctyl sulfosuccinate (AOT). After separation from the microemulsion, the nanoparticles of about 10nm were calcined and the growth process was monitored. Transmission Electron Microscopy (TEM) results show that the irregular precursor nuclei will tend to form cubic shape and the particles grow larger to 20-30nm when the calcinations temperature is increased to 600°C. Lower temperature and longer calcination duration were favorable for the formation of monodispersed smaller particles. X-ray Diffraction (XRD) confirmed the crystalline nature of the ferrite particles. The compositions of the products was found to be determined by both the feed ratio of metal salts and the pH values of the microemulsion, which were analyzed through X-ray Photoelectron Spectroscopy (XPS) and Elemental Analysis. The magnetic properties of the nano-ferrites were measured using a Superconducting Vibration Sample Magnetometer (VSM). The cobalt ferrites nanoparticles synthesized had a relatively high coercivity (1555 Oe) and a saturation magnetization (77.32emu/g). The relationship between the magnetic properties and the crystal structure as well as the domain size will be discussed.

10:00am **MI-FrM6 Measuring Drive and Media Performance using Quantitative Analysis of MFM Images***, **D.A. Chernoff**, D.L. Burkhead, C.S. Cook,* Advanced Surface Microscopy, Inc.

MFM imaging of magnetic hard disks provides a direct physical examination of magnetic marks that complements electrical measurements made on test stands. Valuable information can be obtained because the MFM is free of interference from cross-talk and other read head limitations. Such images have mostly been used for qualitative analyses, such as bit shape, erase band structure, and missing information (defects). However, quantitative analysis of track and bit position and of bit signal amplitude can provide important information to aid in the design and engineering of higher density drives. To assess the accuracy of disk drive servo tracking or of the disk servo writer, we captured several MFM images, each showing 10-15 tracks in the data or the servo mark areas of an ordinary disk. We have demonstrated that our proprietary method@footnote 1@ for calibration and measurement can measure track pitch with precision better than 0.3% (1 s.d.) on calibration specimens and on optical discs.@footnote 2@ For data tracks on a magnetic disk, track pitch variation (1 s.d.) was 3% of the mean track pitch. Drive system engineers can use this information to set target values and tolerances for track pitch. To assess media performance and noise, we captured images of a special test disk, written with constant frequency test patterns. Using similar tools, we analyzed the bit position and amplitude data. Bit position variation (1 s.d.) was 1.5% of the bit spacing and bit amplitude variation was 6.3% of mean amplitude. The variation in bit position (jitter) and in bit amplitude are fundamental sources of digital errors and can be a figure of merit for media response at a given spatial frequency. @FootnoteText@ @footnote 1@ MagneTrack and DiscTrack Plus Media Measurement Systems, www.asmicro.com. @footnote 2@ Automated, high precision measurement of critical dimensions using the Atomic Force Microscope, D. A. Chernoff and D. L. Burkhead, J. Vac. Sci. Technol. A 17, 1457 (1999).

10:20am **MI-FrM7 Femtosecond Spin Dynamics in Ferromagnetic Layered Systems***, **B. Koopmans**,* Eindhoven University of Technology, The Netherlands **INVITED**

Ultrafast spin dynamics in ferromagnetic metals is an issue of great current interest. Pump-and-probe pulsed laser techniques have been successfully applied to study magnetism down to femtosecond time scales. Several groups have reported on an almost instantaneous (< 100 femtosecond) loss of magneto-optical contrast in nickel and cobalt films after excitation by a short laser pulse.@footnote 1@ These observations have triggered fundamental discussions as to the ultimate magnetic time scales, and the responsible scattering processes. In this presentation an introduction to time-resolved magneto-optical techniques and an overview of the rapidly developing field will be presented. In particular, it will be shown that ultimate care has to been taken in the interpretation of these experiments. Using a novel configuration we were able to demonstrate that during the first hundreds of femtoseconds a direct relation between magneto-optics and magnetism in ferromagnetic nickel does not exist. Nevertheless, using the distinct temperature dependence of the true demagnetization and that of optical artifacts, such as state-filling effects, we have been able to access the genuine magnetization dynamics. In our experiments on epitaxially grown Cu/Ni/Cu wedges evidence was found that the equilibration of the electron and spin systems takes place within approximately 0.5-1 picosecond. Oscillations on a much slower time scale, hundreds of picoseconds, were interpreted as a precession of the magnetization vector, triggered by the optical heating pulse. The latter phenomenon may be applied as all-optical real-time ferromagnetic resonance for the investigation of magnetic devices with a sub-micrometer spatial resolution. . @FootnoteText@ @footnote 1@ See e.g. E. Beaurepaire et al., Phys. Rev. Lett. 76, 4250 (1996); J. Hohlfeld et al., Phys. Rev. Lett. 78, 4861 (1997); J. Gadde et al., Phys. Rev. B 59, R6608 (1999).

11:00am **MI-FrM9 Magnetic Force Microsopy on Inductive Recording Heads***, **A. Moser**, M.E. Best, D.K. Weller,* IBM Almaden Research Center

Magnetic Force Microscopy (MFM) has been used to characterize the magnetic stray field generated by the inductive write elements of heads as a function of the amplitude and the pulse width of the write current. The permeability of the write element has been quantified by energizing the head with an offset current that is modulated with a sinusoidal waveform. This current modulation leads to a periodic change in the resonance frequency of the cantilever which has been monitored using a lock-in amplifier. 2D maps of the cantilever resonance frequency show that the write head first saturates at the gap. The saturation current is discussed for different materials and physical structures of the write poles. In a second experiment, the energizing current has been additionally pulsed with pulse widths as short as few nanoseconds to measure the high-frequency behavior of write heads. Here, we observe that larger write current are needed to saturate the write heads at higher frequencies.

11:20am **MI-FrM10 Surface Processing with Gas Cluster Ions to Improve GMR Films***, **D.B. Fenner**, J. Hautala, L.P. Allen, J.A. Greer, W.A. Skinner,* Epion Corporation*; A. Al-Jibouri,* Nordiko Limited, England*; J.I. Budnick,* University of Connecticut

Reduction of roughness and removal of contamination on surfaces of substrates and films for giant magneto-resistance (GMR) will be essential in the development of advanced devices. Tools and methods to accomplish this are limited at present. Gas-cluster ion beam (GCIB) technology shows promise as a dry process that can provide substantial improvement, and can be integrated into GMR-film deposition-and-etch tools. Here we describe recent work developing GCIB techniques and processes for tantalum, alumina, copper, permalloy and other types of GMR-device films relevant to the spin valve, tunneling-MR (TMR) and nano-oxide layer (NOL) technologies. With argon GCIB it is possible to reduce the roughness of tantalum films to well below a nanometer (rms), and the roughness falls exponentially with dose. The exposure to GCIB rapidly reduces the presence of asperities on surfaces and removes other contamination. @FootnoteText@ Supported by NIST-ATP.

11:40am **MI-FrM11 Study of Exchange Anisotropy of Ni@sub 80@Fe@sub 20@/Fe@sub 60@Mn@sub 40@(111) Epitaxial Films@footnote 1@***, **C. Liu**, G.J. Mankey,* University of Alabama

Ferro-antiferromagnetic interfacial exchange anisotropy has been studied extensively.@footnote 2,3@ We have grown Ni@sub 80@Fe@sub 20@/Fe@sub 60@Mn@sub40@ fcc (111) films on epitaxial Cu(111) buffer layers on Si(110). With increasing Cu buffer layer thickness, LEED and RHEED show improving film crystal quality while atomic force microscopy reveals an increase in interfacial roughness. Films with Cu buffer layers thinner than 10 nm had coercivities less than 13 Oe, and the exchange anisotropies deduced from the hard axis initial susceptibility were consistent with the results of hysteresis loop measurements. Films with thicker Cu buffer layer had coercivities and exchange anisotropies deduced from hard axis initial susceptibility that were larger than the results of hysteresis loop measurements. For all films, the angular dependencies of exchange bias H@sub eb@ were not sinusoidal, and surprisingly, all films showed a deviation of pinned direction from the direction of the applied field during film growth. Specifically, the film with thickest Cu buffer layer (100 nm) had the largest deviation (57Â°). This film also exhibited the largest coercivity (47 Oe). Magnetic force microscopy measurements showed a strong ripple pattern for this film, with a length scale of 2 microns, characteristic of a strong stray field in the film. All the results revealed the inhomogeneous nature of the pinning in the films which is closely related to the canting of interfacial spins. We interpret these results based on the combination of effects of roughness and structure induced change of intrinsic magnetic properties. @FootnoteText@ @footnote 1@Funded by ARO #DAAH 04-96-1-0316 and NSF #DMR-9809423. @footnote 2@A.E. Berkowitz and Kentaro Takano, J. Magn. Magn. Mater. 200, 552(1999). @footnote 3@Joo-Von Kim, et al., Phys. Rev. B 61, 8888(2000).

MEMS
Room 309 - Session MM+VT-FrM
MEMS Actuators, Pumps, Power Devices, and Tribology

Moderator: R. Robbins, Texas Instruments

8:20am **MM+VT-FrM1 Micromechanical Devices for Force Measurement***,* ***T.W. Kenny,*** Stanford University **INVITED**

In recent years, many researchers have adapted lithography, deposition and etching techniques from the IC processing community to the fabrication of micromechanical sensors. Many of the signals that these sensors are intended to detect are expressed as forces which stress or deflect the micromechanical structure. As sensors are miniaturized, these forces naturally become smaller, and techniques for detection are required to improve. Our research group has been engaged in a variety of activities, all of which share an interest in improving the force detection capability of microinstruments. In this talk, an overview of these activities will be presented, beginning with simple strain-gauge sensors (micronewtons), sensors based on tunneling displacement transducers (nanonewtons), AFM cantilevers (piconewtons), and ultra-thin force sensing cantilevers (attonewtons). Opportunities for exciting scientific measurements will be highlighted, and challenges for application of MEMS devices to these measurements will be discussed.

9:00am **MM+VT-FrM3 Developing MEMS Vacuum Pumps***,* ***E.P. Muntz,*** University of Southern California **INVITED**

There are no satisfactory MEMS vacuum pumps; particularly unavailable are vacuum pumps that can handle the flow required for MEMS scale, continuous sampling instruments. The two obvious paths to creating such pumps, adapting current technology to MEMS scales or inventing new MEMS friendly technology, are discussed. The first path has been tried to some extent and not been successful, the second has been studied and a few possibilities are under investigation. A generic scaling study of expected trends in vacuum pumping performance as size is reduced to the MEMS scale is presented. It indicates that in practically all cases present vacuum pumps scaled to MEMS dimensions are not very attractive. New technologies that may offer more attractive possibilities are discussed. The degree of attraction is measured in terms particularly applicable to MEMS devices; the energy required per unit of upflow in the pump and the pump volume per unit of upflow. Both of these need to be sufficiently small to permit self consistency in energy use and size in order to allow local integration of the pumps with the MEMS devices that require vacuum pumping. For instance the full potential of instruments such as a MEMS sampling mass spectrometer can only be achieved if the pumps have power or space requirements equal to or preferably significantly less than the instrument itself. It is concluded that with new pumping technologies that have been identified, it may be possible to provide satisfactory MEMS vacuum pumping performance. However, this will only come to pass if a determined research and accompanying development program is created.

9:40am **MM+VT-FrM5 Miniaturized Fuel Cell for Portable Power***,* ***H.L. Maynard****, J.P. Meyers,* Lucent Technologies, Bell Laboratories

We are developing a silicon-based miniaturized fuel cell to power 0.5-20 W portable telecommunication, computing, and personal entertainment devices. Fuel cells provide a 5-10x improvement in energy storage over advanced rechargeable batteries, allow "instant recharge" (with the insertion of a fuel cartridge), and enable sustained operation away from the power grid. The fuel cell is a methanol-based proton-exchange membrane (PEM) device. Our design is implemented in silicon to leverage advanced silicon processing technology, expertise and facilities. Applying silicon processing techniques to the fuel cell structure enables precise control over the thin-film properties and interfaces, enabling optimization of the critical three-phase region of ionic conductivity, electronic conductivity and gas and/or fluid permeability. Additionally, using a wafer-based approach minimizes production costs, instead of individually constructing and assembling the components. The advantages and disadvantages of two designs will be discussed: a two-wafer bipolar design and a single-wafer integrated monolithic structure. We discuss key integration issues including: thermal management, water control, air movement, fuel delivery, and power conditioning. We will also present preliminary experimental results.

10:00am **MM+VT-FrM6 Nanotribology and Stiction Studies of Surface Micromachined Electrostatic Micromotors Using An Atomic Force/Friction Force Microscope***, S. Sundararajan,* ***B. Bhushan,*** The Ohio State University **INVITED**

Microelectromechanical systems (MEMS) which involve relative motion often encounter tribological problems that undermine and sometimes even prevent device operation. One such problem is that of static friction or stiction. An atomic force/friction force microscope (AFM/FFM) allows for direct measurements on fabricated devices, components and their surfaces. The AFM can be used to study tribological properties of surfaces that exhibit stiction. Nanotribological studies have been conducted on surface micromachined polysilicon micromotors for the first time using a commercial AFM/FFM. Surface roughness parameters (RMS, peak-to-valley distance, skewness and kurtosis) and nanoscale adhesion and friction properties of various surfaces of the motor were measured. Different surfaces of the motor components exhibit different surface roughness and friction properties. A novel technique to measure the stiction encountered in these motors using an AFM has been developed and is described. Using this technique, the effects of humidity and rest time on stiction in the motors have been studied. The mechanisms responsible for stiction in such devices are discussed. Meniscus forces between the mating surfaces of the motor may be the cause of the observed stiction. The real area of contact between the mating surfaces is an important factor affecting meniscus forces. The use of perfluoropolyether (PFPE) liquids as lubricants to reduce friction and stiction for such MEMS devices is investigated.

10:40am **MM+VT-FrM8 Characterizing Coupled MEM Oscillators for Array Applications***,* ***R. Baskaran,*** Cornell University*; K.L. Turner,* University of California, Santa Barbara

MEM Oscillators have been successfully used as accurate sensing and actuation elements. We present a system of electrostatically coupled (by interdigital placement of the movable combfingers) torsional MEM oscillators. This design aims at studying the electrostatics of torsional systems and dynamics of variable coupling strength oscillators for distributed systems applications.@footnote 1@ The configuration allows design of elements with out-of-plane motion at locations across a large area without long springs/suspended structures, eliminating complex modes of oscillations close to operating frequencies and processing issues of large released structures. By design, each of the oscillators can be used for either capacitive sensing or actuation,like in a distributed control network. With integrated tips, the present design also lends itself to applications like AFM/STMs. We have designed, fabricated (with the SCREAM process) and characterized a 2-oscillator system. A high-accuracy(~4nm) laser vibrometry technique is used to get phase and amplitude of the displacement and velocity for various forcing voltages. Experiments have been performed to extract the electrostatic and dynamical parameters (represented by a coupled harmonic model) of the system. Experimental results show a near complete energy sharing (equal area under the Amplitude-Frequency curve) between the two oscillators in the primary resonance.'Beat' phenomenon i.e Amplitude modulation, typical of coupled systems, was observed in the impulse response as well as in the amplitude 'build up' to resonance. The phase relationship between the two oscillators will be useful to characterize the coupling mechanism and is presently under investigation. Future work involves extending the system to multiple oscillator arrays. @FootnoteText@ @footnote 1@Gabriel.K., Jarvis.J., Trimmer.W "Small machines, Large opportunities" Micromechanics and MEMS Classical and Seminal papers to 1990(IEEE).

11:00am **MM+VT-FrM9 Tunable Mechanical Oscillator***, **M.K. Zalalutdinov**, B. Ilic, A. Zehnder, J.M. Parpia, H.G. Craighead,* Cornell University

It has been demonstrated that cantilever beam can resonate at various frequencies when driving force is applied locally, at different points along the beam. The tip of a scanning tunneling microscope (STM) engaged at the cantilever surface is driven in the Z-direction, acting as driving point-source with a subAngstrom amplitude. Cantilever motion was detected by the Scanning Electron Microscope incorporated into a UHV STM system and a spectrum analyzer was used to monitor the modulation of the videosignal, actuated when electron beam crosses the vibrating cantilever. Low stress silicon nitride cantilevers were fabricated using conventional bulk silicon micromachining techniques and coated with a 300Å Au/Pd film in order to provide good tunneling conditions. In this paper we present the results obtained with a 225x20x0.6 µm cantilever. When the driven STM tip was positioned above the bulk part of the sample, near the base of the beam, the conventional cantilever mode was excited with the resonant frequency 9,7kHz. When the STM tip is moved so that it engages the cantilever surface, an additional local constraint is placed on the beam's motion, altering the vibrational mode and causing the shift of the eigenfrequency. We detected a continuous increase of the resonant frequency (up to 25kHz) as the STM tip was moved along the center line from the base to the middle of the beam. This continuous variation of the resonant frequency has numerous possible applications, and was accomplished without a significant change in the Q. We have analyzed the measured deflection vs position using a model of the beam motion and found good agreement over the range we have studied. Possible realization of tunable micromechanical oscillators, based on the concept of a drive induced by the application of the local stress will be discussed.

11:20am **MM+VT-FrM10 Thermal Characteristics of Microswitch Contacts***, **X. Yan**, N.E. McGruer,* Northeastern University*; S. Majumder,* Analog Devices*; G.G. Adams,* Northeastern University

Electrostatically actuated microswitches and relays have been developed at Northeastern University.@footnote 1@,@footnote 2@ Devices are approximately 100 @micron@ x 100 @micron@ in area and operate with an actuation voltage of 50-60 V, corresponding to a contact force of 100-150 microNewtons. The contact resistance varies less than 0.5 @ohms@ over 10@super 7@ cycles, with 4-10 mA current cold-switched. Switches have also been tested up to 10@super 9@ cycles with less than 0.5 @ohms@ variation in contact resistance, and with 330 mA of current for up to 18 cycles. The contacting bodies are a "drain" electrode approximately 0.2 @micron@ thick, and a pair of cylindrical bumps 1 µm in radius protruding from a 6 µm thick cantilever. The actual contact area is much smaller and consists of one or more small asperities. In this paper we study the microswitch contact properties at high currents. Finite element electrical and thermal models have been developed using ANSYS, and the modeled current handling limits are compared with experiments. Modeling shows that for a range of switch designs with thin-film drains, the highest temperature is located within the drain rather than at the contact interface, and this location moves further away from the contact interface as the drain thickness decreases or the length of the drain trace increases. Experiments confirm these trends, and show that switches fail catastrophically due to evaporation of the drain trace metal. SEM analysis of contact surfaces at various current densities is also presented. SEM analysis shows that even at the highest currents at which the trace metal evaporates, the contact surfaces typically show relatively little damage, mainly material transfer from one contact surface to the other. @FootnoteText@ @footnote 1@ S. Majumder, N. E. McGruer, "Study of Contacts in an Electrostatically Actuated Microswitch", Proceedings of 44th IEEE Holm Conference on Eletrical Contacts, pp 127-132 (1998) @footnote 2@ P.M. Zavracky, S. Majumder, and N.E. McGruer, "Micromechanical Switches Fabricated Using Nickel Surface Micromachining," J. Microelectromechanical Systems, Vol. 6, pp 3 (1997)

Manufacturing Science and Technology
Room 304 - Session MS-FrM

Langmuir Award/Ultra Clean Society and Contamination Free Manufacturing

Moderator: A. Diebold, Sematech

8:20am **MS-FrM1 Surfaces, Interfaces, and Chemical Reactions in Semiconductor Technology and Manufacturing***, **G.W. Rubloff**[1],* University of Maryland **INVITED**

Atomic-scale properties and chemical reactivity of surfaces and interfaces constitute the science upon which semiconductor technology advances. Since thin film growth, etching, and modification occur as dynamic sequences of surface or interfacial reaction steps, surface reaction phenomena indeed determine the morphology, topography, microstructure, and chemical/physical properties of microelectronic structures, as well as their resulting functionality in devices, circuits, and systems. The surface science community brings an invaluable set of research strategies to understand, control, and advance semiconductor technology, particularly in combining vacuum technology and highly controlled process conditions together with surface, interface, gas phase, and thin film materials characterization. These synergies are proving effective as well in addressing key issues in semiconductor manufacturing.

9:00am **MS-FrM3 The Application of In-situ Monitor of Extremely Rarefied Particle-clouds Grown Thermally Above Wafers by using Laser Light Scattering Method to the Development of the Mass-production Conditions of the Tungsten Thermal CVD***, **N. Ito**, T. Moriya, F. Uesugi,* NEC Corporation, Japan*; S. Moriya, M. Aomori, Y. Kato,* Tokyo Electron Ltd., Japan*; M. Tachibana,* Tokyo Electron Yamanashi Ltd., Japan

It is successfully demonstrated that the scattered-light intensity by thermally grown particle-clouds above wafers in the real tungsten (W) CVD chamber has a good correlation both with the surface roughness of the W-CVD film measured by the atomic force microscopy (AFM) and with the raw material gas-flow ratio SiH@sub 4@/WF@sub 6@. In addition, since our in-situ particle monitor above wafers can detect particle-clouds consisting of particles less than 10nm in size, the appearance and the motion of particle-clouds corresponding to the transient variation of the ratio SiH@sub 4@/WF@sub 6@ at the conversion of gases and/or at the change of the flow rate can be observed. On the basis of these results, the mass-production conditions of particle-free and smooth surface of W-films are clarified with short Cycle Time. The traditional ways of developing the mass-production CVD conditions need many monitor-wafers and are time consuming, because both clarification of the suppression conditions of gas-phase particles by the in-situ particle monitor in vacuum exhaust lines and confirmation by the wafer-level visual inspection are indispensable. Moreover, the sensitivities of in-situ particle monitor at an exhaust line and the wafer-level inspection machine become insufficient to develop process conditions, as reduction of design rule for LSI proceeds. Therefore, application of the in-situ particle monitor above wafers to the development of mass-production conditions is notable method to minimize the non-product wafers and to realize short Cycle Time.

9:20am **MS-FrM4 Standard Practice for Temperature Calibration of the Silicon Substrate in Temperature Programmed Desorption Analysis***, **T. Matsunaga**,* Matsushita Inc., Japan*; N. Yabumoto,* NTT Adv. Tech. Co., Japan*; N. Hirashita,* Oki Electric Ind. Co., Ltd., Japan*; H. Okumura,* Toray Res. Center, Inc., Japan*; M. Nishiduka,* Toshiba Corp., Japan*; I. Nishiyama,* NEC Corp., Japan*; M. Matsuura,* Mitsubishi Corp., Japan*; M. Morita,* Osaka Univ., Japan*; A. Shimazaki,* Toshiba Corp.*; T. Jimbo,* Hitachi, Ltd.*; T. Ajioka,* NTT Electronics Corp.

Ultra Clean Society (UCS)'s Equipment Standardization Working Group proposed a standard practice covering temperature calibration of the silicon substrate, ranging from 400 to 1000°C, for temperature programmed desorption (TPD) analysis. Although TPD has been widely used to characterize materials and fabrication processes in ULSI devices, the temperature is not accurate enough to develop reliable fabrication processes. The desorption temperature was found to differ over 100°C between interlaboratory TPD measurements. In order to solve this problem, the ramping temperature of TPD instrument was calibrated to silicon substrate temperature by this proposed standard practice, which consists of heating silicon calibration materials at a controlled rate in TPD instrument, measuring characteristic desorption peak temperatures, and quadratic calibration fitting to the standard temperatures. The calibration

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[1] **Gaede-Langmuir Award Winner**

materials are (1) CaC@sub 2@O@sub 4@.H@sub 2@O dropped on a Si wafer and dried, (2) Ar and (3) H ion implanted into Si wafers. The standard temperatures of the characteristic desorption, associated with decomposition, structural transformation and lamination of silicon, were determined by special TPD instrument with the highest isothermal space around the specimen among the interlaboratory. The precision of this practice was determined in an interlaboratory test in which 4-5 laboratories participated using two instrumental models. This test using a few common specimens proved that the average standard deviation, measured in different laboratories for all the measurements with ramping rates of 10, 30 and 60°C /min, was estimated to be 6.0°C between 400 and 1000°C.

9:40am **MS-FrM5 Standardization of the Method to a Disiloxane Concentration in Monosilane Gas using Atmospheric Pressure Ionization Mass Spectrometer**, ***M. Kitano,*** Tohoku Univ., Japan; *Y. Sakakibara,* NTT Adv. Tech. Corp., Japan; *Y. Ishihara,* Nippon Sanso Corp., Japan; *Y. Kunii,* Kokusai Electric Co., Ltd., Japan; *K. Hasumi,* Hitachi Tokyo Electronics Co., Ltd., Japan; *I. Matsuda,* Syowa Denko K.K., Japan; *A. Ohki,* Osaka Sanso Kogyo Ltd., Japan; *Y. Shirai,* Tohoku Univ., Japan

Ultra clean society (UCS)'s process gas measurement standardization working group proposed, using atmospheric pressure ionization mass spectrometer (APIMS) which has two ionization compartments to measure the disiloxane(SiH@sub 3@-O-SiH@sub 3@) in monosilane(SiH@sub 4@) gas at concentrations between 10ppb to 1000ppb. In this standard, SiH@sub 4@ with SiH@sub 3@-O-SiH@sub 3@ of unknown concentration is introduced into the second ionization compartment. Ar@super +@ ion generated by corona discharge in the first ionization compartment is sent out to the second ionization compartment. And Ar@super +@ ion reacts with SiH@sub 3@-O-SiH@sub 3@ in the SiH@sub 4@ gas to exchange ion, and SiH@sub 3@-O-SiH@sub 3@ ion are generated in large amount. SiH@sub 3@-O-SiH@sub 3@ is detected with mass number of 77. Using relative ion intensity of SiH@sub 3@-O-SiH@sub 3@ and calibration curve acquired by follow method, SiH@sub 3@-O-SiH@sub 3@ concentration is determined. H@sub 2@O of a known concentration firstly adsorbed into the stainless steel tube. This tube is purged out using SiH@sub 4@ gas. Adsorbed H@sub 2@O reacts with SiH@sub 4@, and SiH@sub 3@-O-SiH@sub 3@ is generated. Adsorbed H@sub 2@O volume and generated total disiloxane volume are in a proportion of one to one. So that the amount of disiloxane in SiH@sub 4@ gas can be quantitatively calculated. The determination limit, which was defined as 3 times of the standard deviation of SiH@sub 3@-O-SiH@sub 3@ concentration in purified SiH@sub 4@ gas was found to be 10ppb. For verification of calibration curve, calibration curves, which were prepared at different timings and different places by different people, showed good agreement of over 80%. Moreover, it is proved that calibration curve of SiH@sub 3@-O-SiH@sub 3@ in SiH@sub 4@ can be substituted by that of H@sub 2@O in Ar which is corrected with a correction coefficient.

10:00am **MS-FrM6 A Wide Range Vacuum Sensor Fabricated by MEMS**, *H. Miyashita,* ***Y. Kitamura,*** *H. Watanabe,* ANELVA Corporation, Japan; *M. Esashi,* Tohoku University, Japan

A wide range capacitive vacuum sensor has been developed by microelectromechanical system (MEMS) technology. Use of MEMS technology has many advantages such as ability to miniaturization of the sensor, mass production, cost reduction etc. when compared to the conventional mechanical processes. The reason is that MEMS process is very similar to that of semiconductor device fabrication processes. The sensor is comprised of an SD2 glass and a silicon substrate. The length, width and thickness of the sensor is 20mm, 20mm, and 1.4mm, respectively. The fabricated vacuum sensor has two silicon diaphragms with 4mm x 4mm and 1mm x 1mm dimensions, and the thickness of the diaphragms is 7µm. Since the deflection of a diaphragm depends on the diaphragm size, the sensor measures a wide range of pressure. The smaller diaphragm shows linear characteristics of electrostatic capacitance at the pressures below 40,000Pa. The larger diaphragm shows linear characteristics of electrostatic capacitance at the pressures below 200Pa. The developed sensor is able to measure pressure in the range of 0.04Pa to 40,000Pa. This is achieved by using an electrical circuit which converts electrostatic capacitance into voltage over three orders. The same technology is applicable to the fabrication of vacuum sensors that measure pressures in other ranges by changing the size of the diaphragms. Moreover, the number of diaphragms in a sensor also can be increased to enhance the pressure-monitoring region without increasing the fabrication processing steps.

10:40am **MS-FrM8 The Effect of Molecular Weight of Organic Contaminants on their Adsorption on Si-wafers**, ***Y. Wakayama,*** Tohoku University, Japan; *S. Kobayashi, T. Ishii,* Taisei Corporation, Japan; *S. Sugawa, T. Ohmi,* Tohoku University, Japan

It is well known that organic contaminants adsorbed on silicon wafer surface degrade the performance of ULSI devices. However, there have been no reports on relation of adsorption behavior of organic contaminants to the silicon or silicon oxide surfaces and their molecular weight. In this study, we have found that the amount of adsorbates on a silicon oxide suface depends on the molecular weight of organic substances. In order to investigate the adsorption behavior of organic contaminants on silicon oxide surfaces, we used solid waxes with aliphatic hydrocarbons, polyvinyl chloride sheets with phthalic esters and silicone sealing materials containing cyclosiloxanes with different molecular weights(Mw) as a contamination source. Each of these materials was separately stored in a closed vessel with a wafer with oxide film for 24 hours. The above organic adsorbates on the oxide surface were analyzed by thermally desorbed and gas chromatography-mass spectroscopy. It was found from our data that as the molecular weight of the organic compounds on the oxide suface increases the amount of adsorbates from oxide surface increases as well and reaches a maximum. Thereafter the amount gradually decreases down to the detection limit of the instruments. It is thought that the phenomenon is related in some way to the balance between the heat of adsorption of organic substances and the vapor pressure. Because, The heat of adsorption that determines the adsorption ability of organic compounds on Si-wafer increases with increase of Mw. On the other hand, the vapor pressure of organic compounds that also determine their rates of adsorption on Si-wafer decreases with increase of Mw.

Processing at the Nanoscale/NANO 6
Room 302 - Session NS+NANO6+MC-FrM

Nanoscale Spectroscopy

Moderator: L.J. Whitman, Naval Research Laboratory

8:20am **NS+NANO6+MC-FrM1 Identification of Atom Species on Semiconductor Surface Using Noncontact AFM**, ***Y. Sugawara,*** Osaka University, Japan **INVITED**

Recently, the noncontact atomic force microscope (AFM) using frequency modulation (FM) technique achieved true atomic resolution imaging. In order to apply the noncontact AFM as a powerful scientific tool for resolving the atomic features in variety of fields such as materials and biological sciences, it is very important to clarify the imaging mechanisms of the noncontact AFM. The imaging mechanism of the noncontact AFM was not establish clearly, however the investigation concerning the imaging mechanism has been making progress gradually on various surfaces. In this paper, we experimentally investigated the force interaction between silicon tip and Si(111)@sr@3x@sr@3-Ag surface by using the noncontact AFM. In case of reactive silicon tip, the AFM images showed the strong distance dependence dominated by the chemical-bonding interaction due to onset of the orbital hybridization very close to surface. On the other hand, in case of the adsorbed silver atom tip, the AFM images showed no distance dependence, and the individual silver atom on the top most layer of the surface could be resolved, corresponding to the true topography.@footnote 1@ This tip-sample force interaction seems to be dominated by physical bonding interaction such as the van der Waals force between the silver atom on the tip and the silver atom on the surface. These experimental results suggest that the noncontact AFM images drastically change depending on the atom species on the tip apex. It should be emphasized that there is a possibility to identify or recognize atom species on a sample surface using the noncontact AFM, if we can control an atomic species at the tip apex. @FootnoteText@@footnote 1@K.Yokoyama, T.Ochi, Y.Sugawara and S.Morita: Phys. Rev. Lett., 83 (24) 5023, 1999.

9:00am **NS+NANO6+MC-FrM3 Dynamic Polarization Imaging using Heterodyned Electrostatic Forces**, ***D.R. Oliver,*** *A. Pu, D.J. Thomson, G.E. Bridges,* University of Manitoba, Canada

Electric fields at the surface of dielectric materials will produce dipoles related to the polarizability of the material. In this paper we will present a technique that measures the polarization induced by a conducting probe near a surface. The images obtained are derived from the electrostatic forces between the probe and surface. In favourable geometries, the spatial resolution approaches the probe diameter. This measurement technique can be extended to frequencies well above the mechanical resonant fr equency of the probe cantilever by utilizing amplitude modulation heterodyning. Using heterodyning, both time- and frequency-domain forms of this technique can be realized. We expect this technique to be useable up to frequencies of at least 20 GHz and time resolution of 100 ps. We present calculations of the forces generated assuming simple probe geometries and also thermal noise. Experimental results presented compare favourably with these calculations.

9:20am **NS+NANO6+MC-FrM4 Atomic Scale Chemical Identification on Si(111)@sr@3x@sr@3-Ag by Atom Probe-Scanning Tunneling Microscope***, **T. Shimizu**, H. Tokumoto,* JRCAT-NAIR, Japan

A scanning probe microscope (SPM) can determine atomic arrangement of various surfaces. It is, however, difficult to identify the chemical species of the atoms and molecules with the SPM. In order to know the atomic arrangement and its chemical species, there are several trials by combining the SPM with chemical analysis technique such as time-of-flight (TOF) mass spectroscopy and XPS. Spence has first demonstrated the possibility of TOF technique for chemical analysis. Then we have shown the usefulness of the TOF combined system in several cases. Furthermore a group in Delft Univ. has just tried to construct a TOF combined system. Nishikawa's group has already constructed a different kind of TOF. Here we shall present our challenge to atom-by-atom chemical analysis on solid surfaces by combining an Atom Probe of single atom sensitivity with the SPM ability of single atom manipulation (AP-STM). We have already demonstrated the following facts: (1) More than hundred Si atoms transferred from Si surfaces to a W-tip are detected; (2) The transferred Si atoms intermix with the tip material and form silicide; (3) Highly doped arsenic can segregate to the surface layers during annealing, form strange triangular step structure on Si(001) and the ratio of Si to As can be quantitatively determined. In this study, we will demonstrate the single atom identification on Si(111)@sr@3x@sr@3-Ag, whose atomic structure is supported by the Honeycomb Chained Trimer (HCT) model. The model is as follows. The topmost layer is formed by Ag atoms with the HCT arrangement. Below the Ag HCT layer, there is a Si trimer layer. From this model, it is believed that STM bright spots with sample plus voltage correspond to neither Ag nor Si atoms on the surface, but to the center of the triangle formed by three Ag atoms. To confirm the model directly, we are trying to identify the atomic position of Ag by extracting atoms from the surface and detecting the chemical species of extracted atoms.

9:40am **NS+NANO6+MC-FrM5 Tunneling Spectroscopy of Passivated Gold Nanocrystals***, **R.B. Wyrwas**, A.Y. Ogbazghi, T.P. Bigioni, L.E. Harrell,* Georgia Institute of Technology*; T.G. Schaaff,* Oak Ridge National Laboratory*; R.L. Whetten, P.N. First,* Georgia Institute of Technology

Scanning tunneling spectroscopy (STS) and microscopy (STM) have been used to study the electronic structure of small (< 2 nm diameter) alkanethiol-passivated gold nanocrystals. The nanocrystals were prepared via chemical methods, and their mass distribution was characterized by time-of-flight mass spectrometry. STM/STS measurements were done at room temperature, 77 K, and 8 K, with isolated nanocrystals immobilized on Au(111) surfaces by a xylenedithiol self-assembled monolayer (SAM). A histogram of nanocrystal heights measured by STM shows several peaks. These correlate well with distinct peaks in the mass spectrum. STS dI/dV spectra vary with nanocrystal size, and show prominent features due to their quantized density-of-states. Spectra acquired repeatedly over a single nanocrystal evolve in time slowly, possibly due to configurational changes of the nanocrystal or its passivation layer.

10:00am **NS+NANO6+MC-FrM6 Scanning Probe Microscopy Study of Engineered Ferroelectric Domain Structures***, **G. Rosenman**, A. Agronin, Y. Rosenwaks, M. Lesnih, P. Urenski,* Tel-Aviv University, Israel

Ferroelectric domain engineering has recently become an attractive and perspective tool for diverse nonlinear optical applications based on the quasi-phasematching method (QPM). The QPM occurs by the use of specifically tailored ferroelectric domain configurations with alternate direction of spontaneous polarization. Various types of engineered domain structures (periodic, aperiodic and quasi-periodic) allow an effective generation of coherent light in spectral regions where conventional lasers are not available. In this work we have studied engineered domain configurations (fabricated by electrical poling method in ferroelectric KTiOPO4 crystals) using different scanning probe techniques like: piezoresponse imaging, Kelvin probe force microscopy, and conventional topography imaging. The different AFM methods image the periodically poled domains and domain walls with high spatial resolution. A detailed electrostatic analysis of the data, and the contrast between ferroelectric domains with opposite polarity is presented.

10:20am **NS+NANO6+MC-FrM7 Imaging of Single Molecules by Low Energy Electron Point Source Microscopy***, **A. Eisele**, B. Völkel,* Universität Heidelberg, Germany*; S. Rehbein,* Universität Göttingen, Germany*; B. Jäger,* Universität Heidelberg, Germany*; H.J. Kreuzer,* Dalhousie University, Canada*; A. Gölzhäuser, M. Grunze,* Universität Heidelberg, Germany

Low Energy Electron Point Source Microscopy (LEEPS)@footnote 1,2@ has been used for taking in-line holograms of single DNA strands and carbon nanotubes. These two molecules were chosen to elucidate the extend to which the hologram images are determined by structural and electronic properties of the sample. The holograms were analyzed by reconstruction via the Kirchhoff-Helmholtz integral transformation.@footnote 3@ The resulting image is suggested to represent the scattering centers of the molecule, i.e. yielding its atomic structure. However, various effects can impose a limit to the resolution: vibrations between tip and sample, electronic charge deposition on the sample, non-ideal electron coherence, distortion of the electrical field near the sample molecule. It is discussed to which extend such artefacts are visible in the experimental data and whether they constrain the applicability of the Kirchhoff-Helmholtz transform. A comparison between the transformed images of DNA strands and carbon nanotubes shows differences that can be explained by properties of the molecules. @FootnoteText@ @footnote 1@ H.-W. Fink, W. Stocker and H. Schmid, Phys. Rev. Lett. 65, 1204 (1990). @footnote 2@ A. Gölzhäuser, B. Völkel, B. Jäger, M. Zharnikov, H.J. Kreuzer, M. Grunze, J. Vac. Sci. Technol. A16(5), 3025 (1998). @footnote 3@ H. J. Kreuzer, K. Nakumura, A. Wiezbicki, H.-W. Fink, and H. Schmid, Ultramicroscopy 45, 381 (1992).

10:40am **NS+NANO6+MC-FrM8 Atomically-resolved Observation of Single Surface States and Trapped Electrons at Semiconductor Surfaces using Photovoltage Imaging with STM***, S. Aloni, I. Nevo, **G. Haase**,* Weizmann Institute, Israel

Atomically-resolved, super- and sub-band-gap photon surface photovoltage (SPV) imaging was used to study surface states and a trapped exciton at semiconductor surfaces. Super-band-gap radiation that flattens the electronic bands gives rise to SPV that reflects the local band bending in the dark. On the other hand, a sub-band-gap photon can excite a localized electron in a surface state into the conduction band, and produce an SPV that reflects the new charge distribution. By studying the effect of the tip on the local band bending, we can learn about the nature of a single localized surface state on an otherwise surface-state-free surface. It turns out that a single adsorbate or a single atom-size defect, can sometimes screen efficiently a strong external electric field. When a filled deep surface state, such as As-vacancy defect on the surface-state-free GaAs(110) surface, was excited by 1064 nm (sub-band-gap) illumination, a trapped electron state was imaged: It's induced SPV feature had a slight positive value at a radius of ~20 AA, and a negative portion 5-50 AA further away, as expected for a localized positive charge with a wide (bias-dependent radius of 25-70 AA) electron-density distribution around it. An observed six-point star shape of the SPV feature is explained by the contribution of the surface atoms to the potential well shape.

Plasma Science and Technology
Room 310 - Session PS-FrM

Dielectrics II

Moderator: S. Rauf, Motorola Inc.

8:20am **PS-FrM1 Pulsed-PECVD Organosilicon Films for Use as Insulating Biomaterials***, **H.G. Pryce Lewis**,* Massachusetts Institute of Technology*; D.J. Edell,* InnerSea Technology*; K.K. Gleason,* Massachusetts Institute of Technology

Thin films produced by plasma-enhanced chemical vapor deposition (PECVD) have potential application as conformal coatings on implantable devices with complex topologies and small dimensions. Coatings on such devices need to be biocompatible, insulating, and flexible enough to minimize static forces on the surrounding tissue. In this study, we describe the use of pulsed-PECVD to deposit thin films from hexamethylcyclotrisiloxane (D@sub 3@). Pulsed-PECVD is a method in which plasma excitation is modulated to favor deposition from neutral and radical species. Thin, conformal coatings were demonstrated on nonplanar substrates suitable for implantation, such as copper wires and neural probes. Coatings were resistant to prolonged immersion in warm saline solution, and wire coatings produced by pulsed-PECVD showed more flexibility than analogous coatings deposited by continuous-wave (CW) excitation. Using Fourier Transform Infra-Red (FTIR) spectroscopy, it was demonstrated that the mode of plasma excitation is important in determining film structure. Both CW and pulsed-PECVD showed evidence of crosslinking via ternary (T) and quaternary (Q) silicon atoms bonded to more than two oxygen atoms. Methylene groups were observed only in CW films, and may constitute part of a carbon crosslinking unit of the form Si-(CH@sub 2@)@sub n@-Si, where n@>=@1. Methylene was not detectable in the pulsed-PECVD films, suggesting that formation of carbon crosslinks requires a longer plasma decomposition period. The presence of two distinct crosslinking structures in CW films leads to a highly networked structure and results in brittle coatings on thin wires. A higher proportion of terminal methyl groups was also observed in CW films, suggesting that pulsed-PECVD films may retain more precursor ring structure than CW films.

8:40am **PS-FrM2 Kinetic Suppression of Process Gas/Silicon Substrate Reactions During the Remote Plasma-assisted Deposition of Al@sub2@O@sub3@ and Ta@sub2@O@sub5@ on Hydrogen Terminated Silicon Substrates***, **R.S. Johnson**, H. Niimi, J.G. Hong, G. Lucovsky,* North Carolina State University

Deposition of alternative gate dielectrics such as Al@sub2@O@sub3@, Ta@sub2@O@sub5@, Zr(Hf)O@sub2@ and Zr(Hf)O@sub2@-SiO@sub2@ alloys onto H-terminated silicon by chemical vapor deposition, CVD, direct plasma-enhanced CVD, and/or atomic layer deposition, is generally accompanied by subcutaneous growth of interfacial SiO@sub2@ or metal silicate layers that significantly increase equivalent oxide thickness, EOT. Previous studies have shown that silicon substrate/process gas reactions could be effectively suppressed in remote plasma-enhanced CVD, RPECVD, of SiO@sub2@, Si@sub3@N@sub4@ and Si-oxynitride alloys by deposition reaction pathway control. Two aspects of RPECVD contributing to suppression of substrate reactions are i) downstream injection of silicon and metal atom precursors which prevents their fragmentation into reactive species in the gas phase, and ii) fast CVD reactions between unexcited precursors and upstream, plasma-activated oxygen with growth rates > 3-5 nm/minute. Substrate/process gas reactions have been studied by interrupted RPECVD processing-analysis cycles using on-line Auger electron spectroscopy, AES, in a UHV-compatible multi-chamber system. RPECVD of Al@sub2@O@sub3@ and Ta@sub2@O@sub5@ on H-terminated Si, using metal-organic precursors with deposition rates > 5.0 nm/minute effectively suppresses substrate/process gas reactions. Based on AES spectra and capacitance-voltage data, subcutaneous interfacial growth contributes less than 0.5 nm to EOT. In contrast, attempts to deposit ZrO@sub2@-SiO@sub2@ alloys by RPECVD from a Zr(IV)-t-butoxide source at significantly reduced deposition rates, < 1 nm/minute, leads to Si substrate/process gas reactions with Zr silicate subcutaneous interfacial layers adding ~ 1-2 nm to EOT.

9:00am **PS-FrM3 Simulation and Dielectric Characterization of Reactive DC Magnetron Co-sputtered (Ta@sub 2@O@sub 5@)@sub 1-x@(TiO@sub 2@)@sub x@ Thin Films***, **J. Westlinder**, Y. Zhang, F. Engelmark, H.-O. Blom, G. Possnert, S. Berg,* University of Uppsala, Sweden

New capacitor material with high dielectric constant is needed for future integrated capacitor structures. Tantalum pentoxide (Ta@sub 2@O@sub 5@) is considered as one of the most promising candidates. By incorporating titanium into the Ta@sub 2@O@sub 5@ thin film, the already excellent electric and dielectric properties are believed to improve even further. In this work, thin films of (Ta@sub 2@O@sub 5@)@sub 1-x@(TiO@sub 2@)@sub x@ have been grown utilizing reactive DC magnetron co-sputtering of tantalum and titanium in an argon/oxygen atmosphere. By varying the input power to the targets, the composition of the thin film can be controlled. The composition of the films was analyzed with Elastic Recoil Detection Analysis (ERDA) revealing the titanium oxide content (x ranging from 0 to 0.40). The dielectric constant, leakage current and breakdown voltage as well as the refractive index has been measured for different compositions and will be presented. The films are amorphous as-deposited, showing some degree of short range order. To be able to further investigate what influence that has on the dielectric properties of the material, films have been annealed at different temperatures. Data from both simulations and experiments of the dual-target reactive sputtering system will be presented.

9:20am **PS-FrM4 Plasma Enhanced Chemical Vapor Deposition of Zirconium Oxide: Spectroscopic, Material and Device Characterizations***, **J.P. Chang**, B. Cho, D. Bae, L. Sha,* University of California, Los Angeles

As metal-oxide-semiconductor devices continue to shrink in dimensions, high dielectric constant materials such as zirconium oxide@footnote 1@ are needed in both transistor and capacitor structures for improved charge storage and reduced leakage current. In this work, zirconium t-butoxide (Zr(OC@sub 4@H@sub 9@)@sub 4@) is used with O@sub 2@ to deposit zirconium oxide on silicon in a high density Electron Cyclotron Resonance reactor. The gas phase reactions including the decomposition of precursors are investigated using optical emission spectroscopy (OES). Optical emission intensities from the atomic (Zr, C, O and Ar) and molecular species (ZrO, CH and CO) are recorded and quantified as a function of process parameters such as gas flow rates, process pressure, source power, and substrate temperature. Langmuir probe is used to determine the plasma potnetial, the electron density, n@sub e@, and electron temperature, T@sub e@. Various surface analysis techniques including X-ray photoelectron spectroscopy and X-ray diffraction are used to analyze the composition, chemical states, and crystalline structure of the deposited ZrO@sub 2@ films. These measurements are combined to propose realistic gas-phase and surface reaction mechanisms. The effect of in-situ post-deposition annealing on surface composition and film morphology is also investigated at 500-700°C in various ambient, including N@sub 2@, Ar, and O@sub 2@. NMOS transistors and MOS capacitors of a poly-Si(200nm)/ZrO@sub 2@/Si structure are fabricated and tested to determine the dielectric constant, leakage current, I-V and C-V characteristics of ZrO@sub 2@. Moreover, stress induced leakage current and time dependent dielectric breakdown are also investigated to determine the material reliability for the application of ZrO@sub 2@ in microelectronics. @FootnoteText@@footnote 1@ D. J. Hubbard and D. G. Schlom, "Thermodynamic stability of binary oxides in contact with silicon", Journal of Materials Research, 11(11), 2757(1996).

9:40am **PS-FrM5 Etching of High-k Dielectric Zr@sub 1-x@Al@sub x@O Films in Chlorine-containing Plasmas***, **K. Pelhos**, V.M. Donnelly, A. Kornblit, M.L. Green, R.B. Van Dover, L. Manchanda, Y. Hu, M.D. Morris, J.E. Bower,* Bell Laboratories, Lucent Technologies

As new, advanced high-k dielectrics are being developed to replace SiO@sub 2@ in future generations of microelectronic devices, understanding their etch-characteristics becomes vital for integration into the manufacturing process. We report on the etch rates and possible mechanisms for one such dielectric, Zr@sub 1-x@Al@sub x@O (x > 0.2-0.35), in plasmas containing a mixture of Cl@sub 2@ and BCl@sub 3@, as a function of gas composition and ion impact energy. Higher concentrations of BCl@sub 3@ enhance the etch rate as well as selectivity of Zr@sub 1-x@Al@sub x@O etching as compared to the etching of Si, whereas increasing ion energy increases the etching rates but decreases selectivity. In a high density helical resonator plasma, etching rates on the order of 700 Å/min and 1:1 selectivity are typical. Angle-resolved XPS was used to study the composition of the upper ~30Å of the film, before, during and at the end of the etching process. The as-deposited film is found to be enriched in Al near the surface (x>0.5). During etching the surface remains slightly Al enriched (5% over the bulk concentration). The adsorbed B concentration (>50at%) in the surface region far exceeds the gas phase composition (

10:00am **PS-FrM6 CVD BST (Ba@sub x@Sr@sub 1-x@TiO@sub 3@) Etching Characteristics in Inductively Coupled Ar/Cl@sub 2@ Plasma***, **I.-Y. Kwon**, H.-S. Shin, J.W. Kim,* Hyundai Electronics Industries Co. Ltd., Korea

We investigated the etching characteristics of CVD BST film with Ar/Cl@sub 2@ gas chemistry in ICP reactor. The changes of BST etch rate with various etching parameters such as gas mixing ratio, source power, bias power, pressure, and total flow rate were systematically examined. And, electron density, electron temperature, ion density, and plasma potential of Ar/Cl@sub 2@ plasma were measured with L/P, and also representative ions and neutrals in the plasma were analyzed by OES, RGA, and SIMS. XPS was employed for the surface analysis of BST film. Upon varying Ar/Cl@sub 2@ gas mixing ratio, the maximum BST etch rate was observed at 40% Cl@sub 2@. It was generally regarded that Cl@sub 2@ gas assisted BST etching chemically by the formation of some chlorides on the BST surface. XPS results showed that peak shifts including Ti, Ba, Cl were induced by the formation of chlorides. However, Ti remaining on the BST surface was decreased with increasing Cl@sub 2@ gas until 40%, and then saturated above 40% Cl@sub 2@. And, the changes of Ti, Ba, Sr and Cl ions and neutrals with Ar/Cl@sub 2@ ratio showed same saturation tendency by OES and QMS analysis. Therefore, it is estimated that the chemical etch portion of Cl@sub 2@ gas in BST etching is saturated at 40% Cl@sub 2@.

On the other hand, ion saturation current decreased dramatically as the Cl@sub 2@ gas addition to Ar gas, and relative DC-bias and ion energy in plasma decreased with increasing Cl@sub 2@ gas above 40%. Therefore, it is also estimated that the physical sputtering with Ar/Cl@sub 2@ gas ratio rapidly decreases over 40% Cl@sub 2@ addition. Based on these results, it could be thought that the BST etch rate increases by chemical etch portion of Cl@sub 2@ gas under 40% Cl@sub 2@, and then is determined by physical sputtering above 40% Cl@sub 2@ due to the saturation of chemical etch portion. So, we propose chemically-assisted physical sputtering as a etch mechanism of BST film in Ar/Cl@sub 2@ plasma.

10:20am **PS-FrM7 Hardmask Characterization for Polysilicon Gate Patterning***, **F.G. Celii**, C. Gross, S. Detweiler, B. Trentmann, K. Kim, W.D. Kim, H.-Y. Liu, R.T. Laaksonen,* Texas Instruments, Inc.

To pattern sub-0.10 µm structures required for next-generation poly-Si gates, advanced etch techniques must complement current lithography methods. One approach uses photoresist line-narrowing combined with an etch hardmask. 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). We report the characterization of silicon-rich nitride (SRN) and silicon oxynitride (SiON) films used in poly-Si gate patterning. SiON and SRN films were deposited by PECVD in commercial 200 mm reactors. Film composition was measured by RBS and HFS spectroscopies. Typical SiON films contained ~40% Si and O, with ~20% H. Blanket films of 200 3000 Åthickness were characterized optically by FT-IR spectroscopy over 400 - 4000 cm@super -1@ and variable-angle spectroscopic ellipsometry (VASE), over 190 - 1000 nm. The VASE data provides optical constants at lithography wavelengths (193, 248 nm) of the various film compositions. We characterized patterned films by CD swing curves, in which in-line pre-etch critical dimension (CD) measurements are plotted vs. the photoresist (PR) thickness. Reflectivity minima below 1% were calculated using determined optical constants for PR/SiON/Si with SiON thicknesses at 325 Å and ~1000 Å. Etch properties and patterned profiles will also be summarized.

10:40am **PS-FrM8 Selective, Anisotropic and Damage-Free SiO@sub 2@ Etching with a Hyperthermal Fluorine Atom Beam***, **D.B. Oakes**, W.G. Lawrence, A.H. Gelb,* Physical Sciences Inc.

The SIA Roadmap for semiconductors calls for the introduction of neutral beam etching processes in future device generations. Specifically, neutral beam tools are required for silicon dioxide (SiO@sub 2@) etching in the formation of the gate dielectric and contact and via holes. The need for neutral beam tools arises from the combination of space-charge limitations on etch anisotropy and etch induced damage due to the charge content of the beam. The objective of this project is to demonstrate a neutral beam tool that selectively and anisotropically etches SiO@sub 2@. Physical Sciences Inc's FAST@super TM@ plasma technology was used to produce hyperthermal fluorine atom beams with tunable translational energy in the range, 1 to 15 eV. This unique technology accesses an energy range that can facilitate efficient, high rate etching of certain materials without the use of ions that produce damage. The SiO@sub 2@ etching study included the first measurement of the velocity and temperature (20 to 200 C)dependence of atomic fluorine reacting with SiO@sub 2@ in the 1 to 10 eV translational energy range. The data suggests two reaction mechanisms contribute to etching under these conditions. Etching near 1 eV includes a significant thermal component while etching near 10 eV is dominated by a direct process, dependent on the fluorine atom translational energy. Under conditions in which the direct process dominates, anisotropic etching has been demonstrated. Both the selectivity and anisotropy of SiO@sub 2@ etching are dependent on the discharge chemistry. Selectivity ratios of 7:1 for SiO@sub 2@ etching versus both silicon and photoresist were demonstrated. Anisotropies of etching profiles exceeded 20:1. Future work will seek to improve both the selectivity and anisotropy of the process and will address scale-up of the tool for 300 mm wafer etching. Application of the FAST technology to low k dielectric etching based upon organic materials will also be discussed.

11:00am **PS-FrM9 A Downstream Plasma Etching Model Used to Describe the Etching Mechanisms of Low-k Polymers***, **R.R.A. Callahan**, G.B. Raupp, S.P. Beaudoin,* Arizona State University

Future integrated circuit manufacturing will require new materials to yield improved circuit performance and meet increasingly stringent environmental regulations. One novel material under current study is an organic polymer, parylene. Parylene is being investigated as an alternative low-k dielectric material because it offers both environmental and performance advantages over the current dielectric, silicon dioxide. From an environmental perspective, parylene-n is desirable because it can be etched using oxygen instead of perfluorinated compounds (PFCs) typically used for dielectric etching. This will reduce greenhouse gas emissions. From a performance point of view, parylene is a lower dielectric constant material than silicon dioxide. The use of parylene-n may ultimately reduce cross-talk and RC time delays. In lieu of reactive ion etching, downstream etching using a microwave source has been studied in order to characterize the etching mechanism without ion interactions for three different types of parylene; parylene-N, parylene-C, and fluorinated parylene. The apparent activation energy for the etching process has been observed to range from 6.41 to 7.64 kcal/mol at various pressure settings. Etch rate has been determined as a function of pressure ranging from 0.4 to 2.0 Torr and oxygen flow rate ranging from 25 to 225 sccm and applied plasma power of 250 watts. In addition to experimental work, the etching process has been modeled. The total model includes predictions of: 1) the velocity distribution in the afterglow region, 2) the oxygen atom concentration in the plasma, 3) the oxygen atom concentration in the afterglow region, and 4) the oxygen atom concentration at the surface of the sample. The model has been validated using nitrogen dioxide titration. The model validation, the model predictions, and their implications for parylene etching will be presented.

11:20am **PS-FrM10 Surface Studies of the Etching of Low-k Hydrogen SilsesQuioxanes (HSQ) Dielectrics under Medium and High Density Plasma Conditions***, C.N. Ho,* Nanyang Technological University, Singapore*; **C.H. Low**, P. Yelehanka, A. Cuthbertson, A. See, L.H. Chan,* Chartered Semiconductor Manufacturing Limited, Singapore*; G. Higelin,* Nanyang Technological University, Singapore

The need for RC delay reduction, arising from device scaling and increased interconnect complexity, leads to the evolution of vast varieties of low-k inter-metal dielectrics. Doped oxide is the more established group being studied due to its similar composition as SiO@sub 2@. However, issues associated with the film stability, have to be resolved before successful integration of these materials into the multi-level interconnect scheme is achieved. In this work, the chemical aspect of the etching of FOx, one type of SiO@sub 2@-like HSQ materials, is evaluated as part of the feasibility studies towards successful low-k IMD integration. In our previous studies, it was demonstrated that FOx IMD vias can be successfully etched under both medium (MDP) and high density plasma (HDP) conditions. Comparative studies on physical performance were performed. Typically, less FOx sidewall bowing was observed in the case of HDP. In addition, higher FOx etch rate and less FOx removal during in-situ photoresist strip (PRS) can be observed. However, higher Si-H loss is induced as shown by FTIR studies. In this work, we perform surface studies using XPS techniques on patterned wafers etched with MDP and HDP source. The surface chemical composition of partially etched TEOS and FOx as well as the post-resist-stripped etched surfaces is investigated through detailed peak de-convolution analysis. In general, higher C1s with negligible Si2p & O1s signal can be observed on both TEOS and FOx surfaces etched under HDP condition. This suggests the presence of a large amount of CF@sub x@ polymer. De-convolution of the C1s signal further indicates difference in the composition, particularly C/F ratio, of polymeric species formed under MDP and HDP condition. After O@sub 2@ treatment, significantly high Si2p and O1s signal can be observed, indicating oxidation of the etched surface. However, in-situ PRS exhibits additional capability in removing the polymer residues.

11:40am **PS-FrM11 Planar-Antenna Structure UHF-ECR Plasma for Highly Selective Insulator Film Etching***, **K. Yokogawa**, M. Izawa, S. Yamamoto, N. Negishi, Y. Momonoi, H. Kawahara, M. Kojima, K. Tsujimoto, S. Tachi,* Hitachi, Ltd., Japan

We developed an ultra-high-frequency ECR plasma (UHF-ECR) etching system with a planar-antenna structure for the etching of insulator film. We believe that high precision radical control, CF@sub 2@/F ratio and CF@sub 2@/ion ratio control of fluorocarbon plasma, is an important for etching of insulator film with highly selective and fine feature control for below 0.13 µm design rule ULSI devices. UHF-ECR has a function of the radical control that is achieved by the plasma gap control for reduction of source gas dissociation and the double-near-surface effect @footnote 1@ for radical changes. A 450 MHz UHF wave was supplied to a planar-antenna located on the opposite side of a wafer. The magnetic field for ECR was supplied by solenoid coils, and distance between the planer-antenna and ECR plane was 5-20 mm. Stable plasma in a wide density range between 10@super 11@ and 10@super 12@ /cm@super 3@ was formed at pressure range between 1 and 50 mTorr. The plasma was uniform within ±3% up to a diameter of 200 mm, and the plasma distribution on the wafer was controlled by the magnetic-field distribution. The SiO@sub 2@ film etching was carried out by UHF-ECR plasma with C@sub 4@F@sub 8@ based gases. We confirmed that the increasing of CF@sub 2@/F ratio can be achieved by the plasma gap reduction using optical emission spectroscopy. We obtained self-aligned-contact etching with selectivity of 25, and high-aspect-ratio-contact hole etching (0.13 µm, aspect ratio: 14) with etching rate above 700 nm/min. High selectivity and high feature control ability were also demonstrated with low-k films such as organic SOG film and organic film. @FootnoteText@ @footnote 1@ S.Tachi, M.Izawa and M.Kojima; 1997 Proceeding of dry process sympo. p.83-90.

Semiconductors
Room 306 - Session SC+EL-FrM
III-Nitride Processing and Devices

Moderator: D.D. Koleske, Naval Research Laboratory

8:20am **SC+EL-FrM1 Process Development For Small-Area GaN/AlGaN HBTs***, **K.P. Lee**, G. Dang, A.P. Zhang, F. Ren,* University of Florida*; J. Han,* Sandia National Laboratories*; W.S. Hobson,* Lucent Technologies, Bell Laboratories*; C.R. Abernathy, S.J. Pearton,* University of Florida*; J.W. Lee,* Plasma Therm

A self-aligned fabrication process for small emitter contact area (2x4 µm@super 2@) GaN/AlGaN heterojunction bipolar transistor is descried. The process features dielectric-spacer sidewalls, low damage dry etching and selected-area regrowth of GaAs(C) on the base contact. The junction I-V characteristics were evaluated at various stages of the process sequence and provided an excellent diagnostic for monitoring the effect of plasma processes such as CVD or etching. A comparison will be given with large emitter-area (2.5x10@super 4@ µm@super 2@) devices fabricated on the same material. The small-area devices are alternative for microwave power switching applications.

8:40am **SC+EL-FrM2 Morphology on HDP-Etched III-Nitride Materials***, T.-N. Kuo, J.-H. Yeh, H.-J. Lee, C.-A. Chen, **D.G.-K. Jeng**,* Nano-Architect Research Corporation, Taiwan

Needle-shaped morphology or highly textured surface was often observed after GaN/GaInN multiple layered structures have been etched in high-density plasma; this phenomenon was not so often observed in structures containing GaN alone. It is attributed to layers containing indium under certain chemical environments. An experimental procedure was carried out for the characterization of materials etching. It turned out that the needle-shaped morphology or textured surface was possibly the consequence of a micro-masking effect due to low-vapor pressure compound formed on the etched surface, which prohibits underneath layers from being etched. The experiments were conducted in a high-density plasma equipment with a novel plasma source designed exclusively by the authoring group. This equipment has the capability for a typical etch-rate of 7000-8000 Å/min for all types of III-nitride compound materials and structures with good surface morphology.

9:00am **SC+EL-FrM3 Effects of Etch Processing on Contacts to n-GaN***, **R. Singh**, C.R. Eddy, Jr.,* Boston University*; H.M. Ng,* Lucent Technologies*; T.D. Moustakas,* Boston University

We report studies on the effects of high density plasma etching on the properties of ohmic contacts to n-GaN. Samples deposited by plasma-assisted MBE on a-plane sapphire and doped with Si are used in this study. Inductively coupled high density chlorine plasmas are applied to etch the surfaces of GaN and subsequent contacts (Ti/Al) to these etched surfaces are evaluated. We identify degradation of contact ohmicity even for very low rf bias powers (ion energies) as a function of the doping level in the GaN film. For films of high doping levels (3x10@super 18@ cm@super -3@), as might be encountered in a laser or LED structure, the degree of contact degradation, compared to the control sample, is a modest factor of 2 (4x10@super -4@ @ohm@cm@super -2@ to 1x10@super -3@ @ohm@cm@super -2@). However, for lower doping level films (10@super 17@ cm@super -3@), as might be encountered in electronic devices, the specific contact resistance is higher by almost two orders of magnitude for the same treatment (5x10@super -3@ @ohm@cm@super -2@ to 2x10@super -1@ @ohm@cm@super -2@). These as-deposited contacts are then rapid thermal annealed (700°C) in a nitrogen atmosphere, where specific contact resistance is monitored as a function of annealing time. Although there is improvement in contact resistivity, the effect of plasma exposure is still evident even at a cumulative rapid thermal annealing time of 280 seconds. We show that even modest ion energies in highly reactive chemistries can lead to contact degradation and that care must be taken in applying such processes if highly efficient power devices are to be routinely realized. In an effort to identify the cause of the degradation, we will also report SEM, AFM and surface sensitive photoluminescence measurements of the as etched surfaces. We will also discuss in-situ and ex-situ efforts to eliminate such degradation.

9:20am **SC+EL-FrM4 Growth of Ga(In)NAs/GaAs Alloys by Plasma-Assisted Molecular Beam Epitaxy***, **A.L. Holmes, Jr.**,* University of Texas at Austin **INVITED**

In recent years, the addition of nitrogen into GaInAs, created via energetic nitrogen species from a RF-plasma or decomposition of hydrazine-based precursors,has attracted a great deal of interest due to the large negative bowing parameter of the resultant semiconductor alloy. As a result, GaNAs/GaAs and GaInNAs/GaAs heterostructures can be grown which emit light at wavelengths applicable for lasers and detectors for fiber-optic communications or absorb wavelengths which make solar cells more efficient. While nitrogen leads to a significant reduction in the band gap of the resultant material, the addition of nitrogen (on the order of a few atomic percent) also leads to a significant reduction in luminescence intensity which has significant consequences for optoelectronic devices. In this talk, growth of the GaInNAs/GaAs alloy system will be discussed. The effects of important growth-related parameters such as growth temperature, RF plasma conditions, indium composition, and arsenic over-pressure will be described. The resultant materials are characterized by x-ray diffraction, photoluminescence, and SIMS to create a picture of how nitrogen is incorporated and how this incorporation affects the resultant material properties. These properties are then compared to GaNAs-based photodetectors which show outstanding device performance with nitrogen concentrations as high as 2.5%.

10:00am **SC+EL-FrM6 Field Electron Emission and Surface Properties of as-grown and Modified AlGaN Films***, A. Bensaoula, I. Berishev, E. Kim,* University of Houston*; M. Ugarov, V. Ageev, E. Loubnin, A. Karabutov,* General Physics Institute, Russia*; **A. Tempez**,* University of Houston

The correlation between surface morphology and composition, Si substrate orientation and field emission properties of Al@sub x@Ga@sub1-x@N and GaN/AlN films was investigated. It was demonstrated that a high Ga surface density provides thin films with better field electron emission characteristics such as a higher emission current and lower voltage threshold. It was found that a proper choice of the substrate orientation is crucial to obtaining the desired electronic properties since it plays a major role in the resulting thin film surface microstructure. A post-growth modification by X-ray irradiation was also performed on these films. Our results show a significant improvement in the field emission characteristics of the Al@sub x@Ga@sub1-x@N surfaces. The threshold field was reduced by up to three times and current density increased up to 10 A/cm@super2@. These results are consistent with data previously obtained for field emission and laser photoconductivity enhancement by X-ray irradiation of BN thin films. The effect of the X-ray induced generation of additional density of states in the nitride material band gap, on the changes in film conductivity and surface potential barrier height will be discussed. The project was funded in part by a CRDF Grant assistance program (Project # RP0-698), a Russian Federation for Basic Research grant (# 99-02-16653) and a NASA Cooperative agreement #NCC8-127 to the Space Vacuum Epitaxy Center.

10:20am **SC+EL-FrM7 Effect of Annealing and Carbon Concentration on the PL Intensity from GaN:Er and GaN:Eu***, **M.E. Overberg**, C.R. Abernathy, S.J. Pearton,* University of Florida*; J.M. Zavada,* U.S. Army European Research Office, UK

An attractive alternative for emission in the visible and near-IR are rare earth doped III-Nitrides, whose emission wavelength is host-material insensitive and less susceptible to thermal quenching than conventional narrow gap semiconductors. GaN doped with Er and Eu during growth by molecular beam epitaxy (MBE) has been found to produce strong room temperature emission at 1540 nm and 621 nm, respectively. In addition to the electronic characteristics of the host material, impurities such as C and H are expected to play an important role in the emission process. In this study, the effects of carbon doping and annealing in either nitrogen or forming gas on the luminescence intensity from Er-doped and Eu-doped GaN has been investigated. In samples with no added carbon, annealing was found to decrease the room temperature emission. The addition of carbon to the GaN during growth however, not only improved emission relative to non-carbon doped material but also produced material which improved with annealing. For carbon co-doped material the presence of hydrogen in the annealing ambient produced the greatest improvement in emission intensity, suggesting that both C and H are beneficial to the emission process. The effect of annealing on surface morphology and structural quality will also be presented as will a model for the observed PL behavior.

10:40am **SC+EL-FrM8 Probing Nanoscale Electronic Properties in Nitride Semiconductor Heterostructures***, **E.T. Yu**, K.V. Smith, X.Z. Dang,* University of California, San Diego **INVITED**

III-V nitride heterostructures are of outstanding current interest for both optoelectronic and electronic device applications. However, the high concentrations of point and extended defects typically present even in device-quality nitride semiconductor material necessitates detailed characterization and understanding of local structure and electronic properties at atomic to micron length scales for optimization of device performance. In particular, the presence of a variety of defect structures in combination with strong piezoelectric and spontaneous polarization effects in nitride semiconductors leads to pronounced variations in local electronic properties. Experimental characterization, theoretical analysis, and numerical simulation of these effects, especially in the context of nitride heterostructure field-effect transistor (HFET) structures, will be described. Scanning capacitance microscopy has been used extensively to characterize local electronic structure in AlGaN/GaN HFET structures. Measurement and analysis of capacitance contrast as a function of bias voltage allows submicron-scale lateral variations in transistor threshold voltage, nanoscale depleted regions within the channel of the transistor in the vicinity of negatively charged threading dislocations, and evidence of piezoelectric fields arising from local strain in the vicinity of dislocation lines to be observed. Application of large bias voltages during the imaging process is found to give rise to localized trapping of charge in deep levels. Measurement and analysis of the resulting contrast allows the distribution of trapped charge both laterally and as a function of depth to be probed.

11:20am **SC+EL-FrM10 GaN and AlGaN Power Rectifiers***, **A.P. Zhang**, G. Dang, F. Ren, X.A. Cao, K.P. Lee, S.J. Pearton,* University of Florida*; J. Han,* Sandia National Laboratories*; J.I. Chyi,* National Central University,Taiwan*; C.M. Lee, C.C. Chuo,* National Central University, Taiwan

We fabricated the GaN & AlGaN rectifiers and p-i-n rectifiers on a range of different MOCVD-grown materials. The reverse breakdown voltages of lateral GaN&AlGaN rectifiers on 3µm thick resistive GaN&AlGaN were in a range of 2.3~4.3kV with a 30µm Schottky metal and Ohmic metal spacing. The p-i-n diodes on 4µm thick GaN epitaxial layer showed a reverse breakdown voltage of 500V with turn-on voltage of ~5V (100A/cm@super 2@). Different edge termination methods were used to improve the performance of GaN rectifiers, including Schottky metal overlap, guard rings, and float rings and junction barrier control (JBS). The edge termination has a strong effect to prevent catastrophic breakdown at the contact periphery. The lowest R@sub ON@ was 0.14 @ohm@.cm@super 2@ for GaN rectifiers and 2.6 @ohm@.cm@super 2@ for AlGaN rectifiers. Figure-of-merit (V@sub RB@)@super 2@/R@sub ON@ are in the 6 -55 MW.cm@super -2@ range, emphasizing the potential of these devices for power switching applications. For the devices we fabricated, we invariantly observed the negative temperature coefficient for V@sub RB@ most likely due to the influence of defects in the heteroepitaxial GaN. For the similar reverse breakdown voltage, current densities are higher in the p-i-n structures, at the expense of higher turn-on voltage, but the on-voltages still need improvement in the Schottky rectifiers. A comparison will be given with state-of-the-art Si and SiC power rectifiers.

11:40am **SC+EL-FrM11 Growth and Characterization of Gadolinium Oxide Gate Dielectric on Gallium Nitride***, **B.P. Gila**, K.N. Lee, K.K. Harris, W. Johnson, V. Krishnamoorthy, C.R. Abernathy, F. Ren, S.J. Pearton,* University of Florida

Fabrication of high performance metal oxide semiconductor field effect transistors (MOSFETs) on gallium nitride will require both good interfacial electrical characteristics and good thermal stability. While dielectrics such as SiO@sub 2@ and GaGdO have demonstrated low to moderate interface state densities, questions remain about their thermal stability and reliability, particularly for use in high power or high temperature widebandgap devices. In this talk we will discuss the utility of gadolinium oxide, Gd@sub 2@O@sub 3@, as a gate dielectric material on GaN. Gadolinium oxide deposited by gas source molecular beam epitaxy from elemental Gd and an electron cyclotron resonance (ECR) oxygen plasma has been found to produce layers with excellent surface morphologies as evidenced by SEM and AFM, with a surface roughness of less than 1 nm. Surface preparation techniques, both in-situ and ex-situ, have been explored to produce films of different crystal morphologies as evidenced by RHEED and TEM. Stoichiometric films can be easily obtained over a range of growth temperatures, growth rates and oxygen flows. This talk will describe the relationship between deposition conditions and film characteristics for Gd@sub 2@O@sub 3@, and will present electrical characterization and thermal stability of capacitors fabricated from Gd@sub 2@O@sub 3@ on GaN.

Surface Science
Room 209 - Session SS+MC-FrM
Characterization of Oxides and Thin Films

Moderator: J.A. Kelber, University of North Texas

8:20am **SS+MC-FrM1 Characterisation and Microreactor Studies of Nanofabricated Model Pt/Ceria Catalysts***, **C. Werdinius**,* Chalmers University of Technology, Sweden*; O. Hjortsberg,* Volvo Technological Development Corporation, Sweden*; L. Österlund, B. Kasemo,* Chalmers University of Technology, Sweden

In modern automotive catalysts, ceria is an important component for transient storage and release, respectively, of oxygen during lean and rich conditions. In order to study the detailed kinetics of the oxygen storage, well-characterised samples are required. Model catalysts (1 cm@super 2@ sample area) of platinum particles on ceria were nano-fabricated by a novel method called "colloidal lithography".@footnote 1@ Its principal feature is the ability of fast parallel fabrication of almost mono-sized, evenly distributed nano-particles. The manufacturing consists of the following steps; (i) deposit a ceria film on a silicon wafer, (ii) deposit a Pt film of desired thickness, (iii) deposit an array of colloidal particles of desired size and spatial separation, (iv) remove all Pt not shadowed by the particles, using Ar-ion beam etching, (v) remove the particles. The final step leaves an array of Pt particles with size and separation reflecting the colloidal particle size and separation. Samples with different Pt-particle densities and particle sizes (40 and 110 nm) were made, and characterised by several surface analytical techniques, including SEM and XPS. Preliminary results of pulsed CO oxidation experiments in a specially designed microreactor are presented, along with vacuum CO TPD measurements. @FootnoteText@ @footnote 1@ P. Hanarp, D. Sutherland, J. Gold, and B. Kasemo, Nanostructured Materials 12, 429-432 (1999).

8:40am **SS+MC-FrM2 Characterization of Hf and Zr Oxides, Silicides and Silicates, Formed on the (0001) Surfaces of HfB@sub 2@ and ZrB@sub 2@, by AES, XPS, LEED and STM***, **R. Singh**,* University of Illinois at Chicago*; Y. Paderno,* Academy of Sciences of Ukraine*; T. Tanaka,* National Institute for Research in Inorganic Materials, Japan*; M. Trenary,* University of Illinois at Chicago

Transition metal (TM) diborides have comparable and often higher degrees of hardness, chemical inertness and thermal stability than their nitride and carbide counterparts. Therefore, TM-diborides are attractive for the same type of applications as nitrides and carbides such as for hard coatings and diffusion barriers. In order to explore their usefulness as diffusion barriers and gate dielectrics, a series of experiments with silicon were performed. Silicon was deposited by the UHV-CVD of silane gas on clean and oxygen covered HfB@sub 2@ and ZrB@sub 2@(0001) surfaces. On the clean surfaces, HfSi@sub 2@ and ZrSi@sub 2@ were formed. A p(2x2)R30° LEED pattern was observed. The structure of Si on the surfaces was also investigated with STM. On the oxygen covered surfaces, silicates were formed. Oxidation of the crystals leads to the formation of HfO@sub 2@ and ZrO@sub2@, which both exhibited a (3x3) LEED pattern at a high exposure (5 L) and a p(2x2)R30 pattern at a low exposure (0.5 L). Information gained from exposure of oxygen to ZrB@sub 2@ was crucial in interpreting the O 1s region in HfB@sub2@, which partially overlaps with the Hf 4s peak.

9:00am **SS+MC-FrM3 Controlled Coordination and Oxidation State of Copper and Manganese Cations in Complex Nickel-Copper-Cobalt-Manganese Oxide Thin Films***, **D.A. KuKuruznyak**, M.-H. Lee, K.A. Omland, M.C. Gregg, F.S. Ohuchi,* University of Washington

Ionic configuration and cation distribution of the nickel-copper manganite spinels have profound effects on their electrical conduction. As these materials are being widely used for thermistor applications, it is important to find a way of controlling the oxidation states of transition metal cations in these mixed oxides. We have therefore undertaken our research developing a unique method fabricating thermistor composition by chemical solution deposition where cations with unusual coordination and unusual oxidation state can be obtained. Organometallic films deposited on silicon and glass substrates by spin-coating of a liquid precursor solution were decomposed in air at 550°C followed by furnace-annealing at temperatures ranging from 600° to 800°C to obtain single-phase cubic spinel of chemical composition Ni@sub 0.48@Co@sub 0.24@Cu@sub 0.6@Mn@sub 1.68@O@sub 4-x@. XPS, FTIR, and Mossbauer spectroscopy have been used to study oxidation states of transition metal ions. Octahedrally coordinated Cu@super +1@ observed from the specimens (prepared below 700°C) showed unusually large negative binding energy shifts in Cu(2p) peak relative to metallic Cu, of which origin was attributed to the difference in the Madelung potentials. Annealing at higher temperatures causes oxidation of copper to Cu@super 2+@ and reduction of manganese cations from Mn@super 4+@ to Mn@super 3+@. The annealing temperature can precisely control oxidation state distribution of copper and manganese cations.

9:20am **SS+MC-FrM4 Behavior of Lightly Doped-electrons on the Electronic Structure of SrTiO@sub 3@: An Angle-resolved Photoemission Study***, **Y. Aiura**, H. Bando, I. Hase,* Electrotechnical Laboratory, Japan*; T. Yasue,* Tsukuba University, Japan*; T. Saitoh, D.A. Dessau,* University of Colorado

Behavior of lightly doped-electrons on the electronic structure of SrTiO@sub 3@ has been studied using angle-resolved photoemission spectroscopy (ARPES). Two states in the band gap region of SrTiO@sub 3@ (in-gap states) are observed; a state with a sharp Fermi cut-off (metallic state) and a broad state centered at ~1.5eV below the Fermi level (~1.5eV state). In order to study the origin of the metallic state, we have calculated the energy-band of non-doped (stoichiometric) SrTiO@sub 3@ and lightly electron-doped SrTiO@sub 3@ based on the full-potential linearized augmented plane wave (FLAPW) method. From comparison between the calculated results and the experimental ones from ARPES, it was shown that the metallic state can be quite well explained by the rigid-band behavior based on one-electron band theory. For the ~1.5eV state, on the other hand, ARPES spectra showed that there is no visible empirical energy dispersion and that its spectral intensity is very sensitive to the surface condition. These experimental results means that the ~1.5eV state is not caused by the bulk electronic structure, but the surface one due to the surface defects.

9:40am **SS+MC-FrM5 Reactions of Acetaldehyde over UO@sub2@(111) Single Crystal Surfaces: Evidence of Benzene Formation***, **S.V. Chong**, H. Idriss,* The University of Auckland, New Zealand

The reactions of aldehydes on metal oxide surfaces have exposed some of the most exquisite chemistry compared to their alcohol and carboxylic acid counterparts. Due to the intermediate oxidation state of the carbonyl carbon on an aldehyde, reactions such as the Cannizzaro reaction (forming alcohol and carboxylate) and Tishchenko reaction (forming ester) have been observed on various metal oxide surfaces. Furthermore, condensation reactions have also been observed on aldehydes possessing alpha-H atom(s) over stoichiometric metal oxide surfaces, while surface defect sites are able to reductively couple two aldehyde adsorbates to yield alkene. Herein, we present the reactions of acetaldehyde over the stoichiometric, electron irradiated, and H@sub2@ reduced surfaces of UO@sub2@(111) single crystal. TPD results over the three surfaces show evidence of benzene formation, and it appears that electron irradiation slightly increases the conversion to benzene, while H@sub2@ reduction doubles it. Thus, the amount of benzene yield might be a novel way to quantify the extent of surface defects. No C@sub4@ hydrocarbon (crotonaldehyde nor butadiene) traces were observed, indicating that the formation of benzene through aldol condensation pathways might be ruled out.

10:00am **SS+MC-FrM6 Synchrotron-based XPS Study of 1-Decanethiol Chemisorbed on Au(111)***, **Y.W. Yang**,* Synchrotron Radiation Research Center, Taiwan*; L.J. Fan,* National Tsing Hua University, Taiwan*; L.J. Lai,* Synchrotron Radiation Research Center, Taiwan

Self-assembled monolayers have been the subject of intense research due to their potential applications in areas of lubrications, corrosion inhibitions, gas sensors, etc. We combined TDS and synchrotron-based, high resolution core level spectroscopy to study the chemisorption of 1-decanethiol monolayer on Au(111) surface with the molecular films prepared from both gas-phase dosing and solution immersion. On heating to temperatures higher than 400 K, decanethiolate starts to decompose, forming 1-decene via @beta@-hydrogen elimination, and leaves atomic sulfur on the surface. For thin films produced by both methods, S2p core level exhibits a single, well-characterized spin-orbit doublet with S2p@sub 2/3@ at 162.1 eV, indicating identical chemical interaction between sulfur and gold atoms in the films. However, C 1s core level starts from 284.0 eV at low coverage, develops a high-binding shoulder at intermediate coverage and eventually becomes a single peak at 285.0 eV for the high coverage prepared from solution phase. Angle-resolved XPS measurements of substrate core level signal provide a direct measure of the film thickness. The increases of C 1s binding energy is found to be associated with the incomplete final-state relaxation of the carbon atoms due to the thickness increase of the film as the carbon chains tilt toward the surface normal. Moreover, the implication of observing only a well-defined doublet of S 2p signal will be discussed in relation to the sulfur dimer model.

10:20am **SS+MC-FrM7 STM Studies of Pyrrole-sdsorbed Si(111)-7*7 Surfaces***, **Z.L. Yuan**,* National University of Singapore, Singapore

The Si(111)-7*7 surfaces is particularly appropriate in Si surface chemistry, because it contains dangling bonds on several different sites within the surface unit cell, and also STM has been used to provide direct and local information on an atomic scale.@footnote 1@ In the present work, the topographic and spectroscopic analysis of pyrrole adsorption on Si(111)-7*7 surfaces at room temperature under different pyrrole exposures is investigated by scanning tunneling microscopy (STM) and scanning tunneling spectroscopy (STS). No significant changes in the surface reconstruction are observed, some adatoms become dark, however this is not due to the vacancies of Si adatoms, because these adatom are visible under the higher sample bias, the disappearance of adatoms is the result of changes in electronic structure upon reaction with pyrrole. the preservation of the 7*7 reconstruction suggests that the reaction with pyrrole has primarily saturated existing dangling bonds on Si(111)-7*7 surfaces. The adsorption is site selective, the faulted center adatoms are most favored for adsorption among the adatoms. The rest atoms also react with pyrrole from STS observation. Based on our STM/STS and HREELS data, a possible adsorption mechanism of pyrrole chemsorption on Si(111)-7*7 surfaces is also discussed. @FootnoteText@ @footnote 1@R. Wolkow and Ph Avouris, Phys. Rev. Lett. 1988, 60:1049; Phys. Rev. B,1989, 39:5091; J. Yoshinobu et al, Phys. Rev. B 1992, 46:9520; Jpn. J. Appl. Phys. 1993, 32:1171; M. N. Piancastelli et al, Phy. Rev. B 1993, 48:17892,R. A. Wolkow, Annau. Rev. Phys. Chem. 1999, 50:413.

10:40am **SS+MC-FrM8 Characterization of Bound Ultrathin Perfluoropolyether-Functionalized Polysiloxane Films on Silicon Oxide Surfaces***, **F. Parsapour**,* Colorado State University*; D.G. Castner,* University of Washington*; D.W. Grainger,* Colorado State University

Current technological demands for magnetic recording media lubrication include a reduction in the head-disk gap, elimination of stiction, and fabrication of a low adhesion protective surface which can withstand thermal and mechanical stresses associated with hard disk drive operation. Perfluoropolyethers (PFPE) are the most commonly used lubricants in the magnetic recording media. These polymers are typically applied thin films to the hard drive overcoat to which they are generally physisorbed. As a result, they are subject to thermal degradation and "spin-off", ultimately resulting in tribological failure modes. Direct attachment of PFPE films is potentially interesting as a foundation for improved friction and wear performance. We have previously reported fabrication of ultrathin films of polysiloxanes functionalized with perfluoropolyether side chains chemisorbed to surfaces and exhibiting structural anisotropy due to separation of various polymer-grafted components normal to the interface. We now report analogous polymer monolayers but with the important chemical and functional distinction of surface bonding to silicon oxide through alkylsilane anchoring groups. These copolymers were synthesized in a single step through the respective PFPE functional and alkylsilane anchor group coupling reactions. Monolayer films were formed on silicon oxide surfaces through the dip-coating method, resulting in hydrophobic immobilized films ~3 nm thick. XPS measurements support a stratified three-layer film chemistry within the monolayer, and an outer interface enriched with the PFPE moiety. AFM experiments show a high degree of coverage of the oxide surface by the copolymer film, and a relatively uniform surface. LFM measurements exhibit low frictional forces in the areas covered by the monolayer film. Force-displacement curves obtained in a fluid environment reveal a low adhesion surface compared to films prepared from copolymers without the PFPE functional group.

11:00am **SS+MC-FrM9 Aerial Oxidation of Self-assembled Monolayers studied by SIMS, AFM and Contact Angle Measurement***, **N.J. Brewer**, G.J. Leggett,* University of Manchester Institute of Science and Technology, UK

For many applications, the long term stability of self-assembled monolayers (SAMs) is a critical issue. We have undertaken a systematic study of SAM oxidation using secondary ion mass spectrometry (SIMS), atomic force microscopy (AFM) and contact angle measurements. Samples were left in an ambient environment for specific periods of time and then surface analytical techniques were used to observe any changes in the SAMs. SAMs were formed from long and short chain methyl, carboxylic acid and hydroxyl terminated alkanethiols. By using SIMS, we were able to monitor the rate of oxidation. We found that DDT, a long chain methyl terminated SAM, oxidised in seven hours, but the long chain carboxylic terminated SAM was unoxidised after seven hours. This shows that long chain carboxylic acid terminated SAMs exhibit increased stability in air. AFM was used to record the friction coefficients of the SAMs over a period of hours. The change in the coefficient of friction was slow and it was little changed after times when SIMS showed complete conversion of thiolates to sulfonates had occurred. This suggests that although the sulfur-gold bond is broken, the interchain forces still hold the structure together. The collapse of the system is gradual and this is reflected in the slow change in the friction coefficients. Advancing water contact angle measurements exhibited a sharp change in contact angle for carboxylic acid and hydroxyl terminated SAMs due to adsorption of contaminants, but a small change for the methyl terminated SAMs. It is concluded that SAMs may oxidise reasonably rapidly on exposure to air, but that the degradation of their structures and properties is much slower.

Thin Films
Room 203 - Session TF+NS-FrM
Nanostructured Thin Films

Moderator: A. Hosseini-Tehrani, Florida International University

8:20am **TF+NS-FrM1 Cluster Beam Synthesis of Nanostructured Thin Films**, ***P. Milani***, *P. Piseri, E. Barborini, A. Podesta', C. Lenardi,* Universita' Di Milano, Italy **INVITED**

We will present and discuss the use of supersonic cluster beam deposition (SCBD) for the production of nanostructured thin films. With this technique nanostructured films of refractory and semiconductor materials can be produced over large areas on various substrates at room temperature. Elemental building blocks are clusters with a number of atoms ranging from few tens up to few hundreds. These units organize in the film in hierarchical structures from the nanoscale to the mesoscale. By exploiting aerodynamical effects typical of supersonic beams it is possible to obtain very high deposition rates with a control on neutral cluster mass distribution, allowing the deposition of thin films with controlled nanostructure. Due to high deposition rates, high lateral resolution, low temperature processing SCBD can also be used for the micro and nanopattering of cluster-assembled films when little or no post-growth manipulation or assembly is required. As a practical example we will discuss the case of nanostructured carbon films. Surface morphologies, granularity and atomic structure of nanostructured carbon films grown with different precursors and under different conditions have been investigated by different techniques. The application of nanostructured carbon for the fabrication of supercapacitors and field emission devices will be discussed.

9:00am **TF+NS-FrM3 Growth of Regular Arrays of Pillars and Helices with Repeat Distance Below 100 nm**, ***M. Malac,*** University of Alberta, Canada; *R. Egerton,* Portland State University

Oblique deposition onto a rotating substrate pre-patterned with suitable nuclei results in the growth of regular arrays of pillars or helices.@footnote 1@ The repeat distance of such arrays can be varied from below 20 nm to over one micrometer. To improve the control over the microstructure it is beneficial to understand the growth mechanism on a microscopic scale. We find that the helices and pillars (within regular or random-nucleated arrays) are composed of many fibers growing simultaneously. The helix-arm diameter is determined by the number of fibers it contains. The distribution of fiber diameters is very narrow and remains constant along the entire helix height. The fiber-diameter, which is characteristic for given material and ratio of substrate and melting point temperatures, is in the order of a few nanometers. The crystalline nature of the growing material has only a minor influence on the fiber diameter. Additionally, we find that the columns formed within a film deposited onto a stationary oblique substrate are also composed of many individual fibers. The helix- and pillar-size distribution is much narrower within a regular unpatterned (randomly nucleated) array. This can be attributed to regularity of the shadowing between structures within a regular array. Anisotropy of shadowing within a regular square array arises from the varying distance of shadow-providing neighbors as substrate is rotated. This anisotropy has only a minor influence on the final shape of the pillars or helices. The helices within a random array start growth from a single fiber and exhibit a very narrow size distribution before the onset of bifurcation. This narrow size-distribution was observed when the helix arm diameter (= fiber diameter) is below the lower limit of scaling of the thin-film microstructure.@footnote 2@ @FootnoteText@ @Footnote 1@Malac M, Egerton RF, Brett MJ, Dick B, J. Vac. Sci. Technol. B 17 (6), 1999 @Footnote 2@Bales GS, Bruinsma R, Eklund EA, Karunasiri RPU, Rudnick J, Zangwill A, Science 249 (1990).

9:20am **TF+NS-FrM4 Plasma Spray Deposition of Nanostructured Materials**, ***H.M. Meyer, III,*** *R. White,* Oak Ridge National Laboratory; *T.T. Meek,* University of Tennessee

Minimum film thickness achieved with any thermal-spray deposition process is limited by the size of powder feedstock materials. However, nanosized feedstock powder materials can be problematic for current plasma spray gun technology because of agglomeration and gun clogging. Some successes with nanopowder feedstock have been achieved, but mainly using special hardware and low quantities of expensive powders. We report the formation of nanostructured (i.e. nanomaterials) thin films using a unique combination of thermal spray coating techniques and liquid feedstock injection. This advanced thermal spray coating technology is a new method of synthesizing materials tailored at the nanoscale level. Injection of liquids into an arc-plasma gun offers the possibility of forming ultra-thin films at high deposition rates, a long-standing technology goal for the plasma spray industry. The formation of alumina thin films via plasma spray deposition using an aqueous precursor is presented. We compare the properties of our films with films formed by conventional thermal spray deposition using standard commercial alumina powders. Oak Ridge National Laboratory, managed by UT-Battelle, LLC, for the U.S. Dept. of Energy under contract DE-AC05-00OR2272.

9:40am **TF+NS-FrM5 Deposition of Nanoparticles on Metal Surfaces**, ***R.S. Averback***, University of Illinois at Urbana-Champaign; *J.M. Gibson,* Argonne National Laboratory; *K. Albe, C. Zimmermann, Y. Ashkenazy, M. Yeadon,* University of Illinois at Urbana-Champaign **INVITED**

The deposition of metallic nanoparticles on surfaces has been investigated by a combination of molecular dynamics computer simulations and in situ transmission electron microscopy. It was observed that the reaction kinetics were dominated by a combination of interfacial stresses associated with epitaxy and capillary forces deriving from surface roughness. For Cu and Ag nanoparticles, it was found that the interfacial stresses led to 'contact epitaxy,' whereby the first few layers of the nanoparticles came into registry with the Cu(100) surface. Below a critical size, about 4 nm, the entire nanoparticle became epitaxial. For Co nanoparticles, which are more refractory and do not wet Cu(100) and Ag(100), contact epitaxy was not observed, although for deposition at 500 K, the nanoparticles burrowed into the substrate to achieve smoothing and coherency. Additional work examined how nanoparticles and grains in thin films respond to applied stresses. It will be shown that small particles on surfaces slide with little friction when they form a high energy grain boundaries, but that they quickly reorient during sliding and become locked from additional motion.

10:20am **TF+NS-FrM7 Scanning Probe Investigations of Passivated and Bare Au Nanoclusters on H:Si(111)**, ***M.D.R. Taylor***, *P. Moriarty,* University of Nottingham, UK; *M. Brust,* University of Liverpool, UK

Non-contact atomic force microscopy (NC-AFM) and scanning tunnelling microscopy (STM) have been used to characterise the morphology of thin films of decanethiol-capped 6 nm Au clusters spin-coated onto hydrogen-passivated (HF/NH4F treated) Si(111). Prior to cluster deposition, NC-AFM images taken under ambient conditions reveal that the H:Si(111) surface is atomically flat, typically consisting of 30-50 nm wide terraces separated by a mixture of single and multiple atomic steps. Following deposition of passivated clusters onto H:Si(111), a network of branched, dendritic islands (6 nm high) is observed with NC-AFM. The clousters forming these islands are remarkably loosely bound and may be swept aside by the AFM tip to fom agglomerates of clusters via minor modification of the non-contact mode feedback parameters. The underlying layers consist of poorly ordered clusters which are stable under STM imaging conditions with tunnel currentsup to 5 nA. This stability faciltates photon emission STM investigations of the passivated clusters. The results of comparative studies of STM-induced light emission from passivated and bare clusters (and from evaporated Au films) will be presented.

10:40am **TF+NS-FrM8 Nanophase Metal - Metal Oxide Films Deposited from a High-rate, Nanoparticle Beam***, **F.K. Urban III**, A. Hosseini-Tehrani, P.D. Griffiths, A. Khabari,* Florida International University*; Y.-W. Kim, I. Petrov, L. Wei,* University of Illinois

While interest in nanophase films deposited in vacuum from nanoparticle beams dates back to the early 1970s, development of suitable sources for such beams has been difficult. A rapidly increasing number of different materials are now being used to deposit nanophase films, from a few tenths to a micrometer in thickness. The new method employs DC magnetron sputtering and condensation of a conductive target material into a helium and argon gas mixture in a flow rate ratio of up to 0.12 at total pressures between 0.7-0.8 Torr. A low velocity beam of the gas and nanoparticles is formed as they escape through a 3 mm-diameter converging-diverging exit nozzle consecutively into differentially pumped chambers maintained at pressures less than 10-3 and less than 10-4 Torr, respectively. Results to date confirm a typically oxygen-containing nanophase film structure. A set of new metal and doped semiconductor elements including Ag, Al, Au, Co, Cr, Cu, Fe, Mo, Nb, Ni, Pt, Si, Sn, Ta, W, and Zr have just been deposited. To our knowledge, some of these are deposited in vacuum for the first time and details on their nanostructure, composition, and materials properties are just now being learned and will be reported. To date, all films are nanocrystalline with grain sizes ranging from 1 to 20 nm and have a porous structure metallic densities, determined from combined Rutherford backscattering and film thickness measurements, in the range of 15-80% of the bulk densities. The effects of synthesis chamber wall cooling and gas conditions as well as starting material vapor pressure, melting point, and condensation energies will be presented. New findings on material properties will also be presented.

11:00am **TF+NS-FrM9 Thin Film Growth on a Fullerene Molecule***, **T.P. Martin**,* Max Planck Institut FKF, Germany **INVITED**

Since the surface of a fullerene molecule is not unlike that of graphite, it might be expected that they have similar properties when acting as a substate for thin film growth. The film-substrate interaction is indeed similar. However, the fact that the fullerene surface is curved and closes on itself leads to interesting differences. Both the similarities and the differences will be discussed including wetting, atom-packing, and reaction between film and substrate.

11:40am **TF+NS-FrM11 Sputtered Fabrication of Periodic Sub-Micron Structures***, **B. Dick**, M.J. Brett,* University of Alberta, Canada

It is known that Glancing Angle Deposition (GLAD) utilizing extreme self-shadowing during film growth can produce periodic microstructures on a pre-defined seed layer with electron beam evaporation.@footnote 1@ This deposition process has been applied to the fabrication of periodic magnetic pillars and has proposed application in optical devices. However, because individual seed elements enforce adatom shadowing on the substrate surface, higher operating pressures, resulting in larger angular flux distributions, can be tolerated in the formation of GLAD microstructures when deposited on a seed lattice. In this presentation, we report the use of low-pressure sputter deposition to fabricate periodic GLAD microstructures of between 500nm and 1.5µm thickness on substrates patterned with a 500nm period seed layer. We have characterized the growth of the microstructures in terms of the target area, deposition pressure, throw-distance, and flux incidence angle. The use of sputtering for periodic GLAD simplifies the process control, and should enable deposition of a broader range of materials for diverse applications including magnetics, optics, and sensors. @FootnoteText@ @footnote 1@B. Dick, M.J. Brett, T.J. Smy, M.R. Freeman, M. Malac, R.F. Egerton. J. Vac. Sci. Technol. A. 18(4), 2000.

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