Monday Morning, October 25, 1999

The Science of Micro-Electro-Mechanical Systems Topical Conference

Room 610 - Session AS+MI+VM-MoM

Magnetic Recording: Chemical Integration and Tribology

Moderator: R.L. Opila, Bell Labs, Lucent Technologies

8:20am **AS+MI+VM-MoM1 Disk Drive Chemical Integration: Influence of Outgassing on Stiction*, D.E. Fowler,*** *R.H. Geiss, E. Ghelichkhani,* Maxtor Corporation **INVITED**

Beyond optimizing the magnetic read/write sensor and the magnetic storage media, the successful introduction of a new disk drive product requires the integration of the best electronics and a great mechanical design to surround this magnetic interface. However, all of this effort will be for naught, if the disk drive cannot spin-up because the interface is stuck together or if contamination at the interface causes the sensor-to-media spacing to be a few nanometers greater than the designed fly height. Failure to spin-up can be the result of stiction and, in some cases, a phenomenon called fly stiction. We briefly discuss the distinguishing physical features of stiction induced by the disk lubricant as compared to stiction induced by in-drive outgassing, before focussing on outgassing-induced fly stiction. Various analytical methods have been used to identify the important outgassing sources and materials within the drive. The formation of liquid droplets on the read/write sensor during drive operation has been documented as an important contributor to increased stiction of the sensor-to-media interface following a period of nonoperation. We describe a real time visualization setup which monitors these processes in experimental, but fully functioning disk drives. This offers the opportunity to study the phenomenon and the mechanisms of fly stiction in a realistic drive environment. Results of these visualization experiments are presented. The goal of these studies is to develop a low-stiction interface through the optimization of the chemical integration of the drive. This allows the high-performance magnetic interface to function according to its design.

9:00am **AS+MI+VM-MoM3 The Evolution of the Corrosion Process on Thin-Film Media*, J. Ying*,** *T. Anoikin, C. Martner,* MMC Technology Inc.

Thin-film hard disks have been exposed to elevated temperature/humidity, and dilute acidic vapor environment. These tests are designed to simulate possible galvanic corrosion, which, for the thin-film media, is characterized by the formation of Co and Ni containing corrosion nodules. The evolution of the corrosion process was elucidated by inducing different degrees of corrosion on the media, and these distinct corrosion stages were characterized morphologically by SEM and chemically by AES compositional analysis. In addition, an XPS chemical state study on the reactivity of Co, Cr, and Ni to ambient and chlorinated environments was conducted. A probable galvanic corrosion mechanism is proposed to understand the chemistry observed during the evolution of the corrosion process. In particular, the effects of ionic contaminants as corrosion accelerators and the role of the Cr underlayer as a corrosion-preventing barrier layer are discussed.

9:20am **AS+MI+VM-MoM4 Tribochemistry of Monodispersed ZDOL with Hydrogenated Carbon Overcoats*, C.-Y. Chen,*** *W. Fong,* University of California, Berkeley*; D.B. Bogy,* University of California, Berkeley, U.S.

Tribo-chemical studies of the lubricant molecular weight effect on the tribology of the head/disk interface (HDI) were conducted using hydrogenated (CHx) carbon disks coated with ZDOL lubricant. The studies involved drag tests with uncoated and carbon-coated Al2O3-TiC sliders and thermal desorption experiments in an ultra-high vacuum (UHV) tribochamber. The studies showed that the lubricant interaction with the carbon overcoat varies as a function of lubricant molecular weight. The friction coefficient increases as the molecular weight increases. The higher friction is due to the higher viscosity. The friction and catalytic decomposition mechanisms of ZDOL are described. In general, the PFPE polymers are decomposed by chain scission involving the breakage of the backbone bonds to yield free-radical segments. Chain scission can occur by three mechanisms: (1) random degradation, (2) depolymerization, and (3) weak-link degradation. Our studies further support previous observations that catalytic reactions occurred at the endgroup functionals. The lower number of endgroup functionals for ZDOL with higher molecular weight reduces the possibility of the occurrence of catalytic reactions. Moreover, the ZDOL desorbed peak temperatures shifted to lower temperatures with increasing molecular weight in thermal desorption tests. The spreading diffusion coefficient of ZDOL decreases with increasing molecular weight. As the mobility of the lubricant chain decreases, the desorption energy needed to break the lubricants increases, resulting in higher desorption peak temperatures. In addition, the longer chain length of the higher molecular weight ZDOL causes higher degrees of crosslinking. The crosslinking restricts chain mobility and causes an increase in the desorption peak temperatures.

9:40am **AS+MI+VM-MoM5 Thermal Effects on Magnetic Head/Disk Interface Materials*, R. Koka*,** Read-Rite Corp.*; L. Zhang,* Seagate Technology, Singapore **INVITED**

The materials interacting at the head/disk interface of a rigid disk drive are primarily the disk carbon overcoat, lubricant on the disk, and the head ceramic,Al2O3.TiC. The interface materials can be subjected to high, localized temperatures when the head is flying or sliding on the disk or when wear debris is trapped in the interface. The head or disk by itself can be exposed to high temperatures during the manufacturing process. This presentation addresses some of the changes that occur in the interface materials when they are individually subjected to high temperatures. Raman spectroscopy of thermally annealed disks will be presented to show that the carbon overcoat tends to become slightly graphitic. At 350C in air, the overcoat oxidizes rapidly and completely disappears. The widely used PFPE lubricants (ZDOL & AM) used on disks, degrade at high temperatures (~350C). In the presence of Lewis acids, the degradation process occurs at lower temperatures (~200C) and the rate of degradation is very high. The products of thermal degradation are different for the two lubricants because of the functional end groups. With respect to tribology, a head made of a passive ceramic such as SiC tends to perform relatively better than a material such as Al2O3.TiC, which is known to be an aggressive catalyst for lube degradation. Annealing of the Al2O3.TiC head ceramic shows that around 350C, carbon diffuses from the TiC grains and titanium oxides are formed. The diffused carbon is amorphous with a mixture of sp2 and sp3 bonds and it becomes nanocrystalline graphite above 600C. Thin, diamond-like, carbon coatings (60A thick) on the surface of the head effectively protect the Al2O3.TiC from oxidation and carbon diffusion at temperatures below 500C. A few examples of disk wear and smear formations on heads and disks will be presented. Some similarities between the Raman spectra of smears on heads and annealed disk overcoats and degraded lubricant will be discussed.

10:20am **AS+MI+VM-MoM7 The Process Induced Changes on the Co-alloy Films and the Tribological Effects on Magnetic Recording Heads*, Y.S. Chaug*,** *R. Adams,* Storage Technology Corporation

The ferromagnetic alloys of Co-metal systems are soft magnetic materials having large saturation magnetization and low coercive force. Sputter deposited Co@sub 1-x@(Zr,Ta)@sub x@ (0.05<x<0.16) amorphous films have been used as magnetic pole material in magnetic inductive heads for its zero magnetostriction. In the wafer process, the Co@sub 1-x@(Zr,Ta)@sub x@(CZT) films were patterned through the photolithography process and then treated with an oxygen plasma for cleaning. The surface changes on the processed CZT surface were studied using x-ray photoelectron spectroscopy. The migration of Co ions to the CZT surface was found after the oxygen plasma treatment. Atomic force microscope, scanning electron microscope and Nano-Triboscope were used to examine the changes of the Co rich CZT surface in a high humid environment. The process induced changes on the CZT surface which impacted the ABS (air bearing surface) lapping process in manufacturing the magnetic inductive heads. The tribology of the magnetic recording heads using CZT as magnetic pole will be discussed.

10:40am **AS+MI+VM-MoM8 Study of Tribochemical Processes at the Head-disk Interface Using Photoemission Electron Microscopy*, S. Anders*,** *A. Scholl, F. Nolting,* Lawrence Berkeley National Laboratory*; W. Fong, C.-Y. Chen,* University of California, Berkeley*; D.B. Bogy,* University of California, Berkeley, U.S.*; C.S. Bhatia,* SSD/IBM*; J. Stohr,* IBM Almaden Research Center

Photoemission electron microscopy (PEEM) has been applied to study the tribochemical processes at the head-disk interface of magnetic storage devices. High resolution PEEM imaging is based on several contrast mechanisms (topographical, elemental, chemical, and various forms of polarization contrast) which makes it a unique tool for the study of tribochemical processes. We have studied surfaces of hard disks and sliders after various kinds of wear tests performed in ambient atmosphere and UHV. It was observed that the disk surface in the wear tracks is chemically modified if visible wear occurred and if a lubricant was present. In the case of unlubricated disks no chemical modifications were observed but a reduction in the hard carbon overcoat thickness. The chemical modifications consist of lubricant oxidation and fluorine removal. The lubricant oxidation and fluorine removal is enhanced with enhanced wear. It was found that degraded lubricant is transferred to the sliders and accumulated in scratches of the slider surfaces. The hard carbon overcoat on sliders was found to be reduced in thickness after the wear tests, but not chemically altered.

11:00am **AS+MI+VM-MoM9 Tribo-Chemistry of the Head-Disk Interface in Hard Disk Drives***, **D.B. Bogy**,* University of California, Berkeley, U.S.*; C.S. Bhatia,* IBM SSD*; C.-Y. Chen, W. Fong,* University of California, Berkeley **INVITED**

Tribo-chemical studies of the lubricant thickness effect on the tribology of the head/disk interface (HDI) were conducted using hydrogenated (CHx) carbon disk samples coated with perfluoropolyether ZDOL lubricant. The studies involved drag tests with uncoated and carbon-coated Al@sub 2@O@sub 3@-TiC sliders and thermal desorption experiments in an ultra-high vacuum (UHV) tribochamber. The studies showed that the lubricant interaction with the carbon overcoat varies as a function of lubricant thickness. Wear durability improves considerably for thicknesses greater than a monolayer. However, in the sub-monolayer thickness regime, the adhesion of the lubricant to the carbon overcoat is much stronger, as indicated by the fact that a much higher temperature is required to desorb the lubricant. When the lubricant thickness is around or above a monolayer, cohesion among the lubricant molecules plays a greater role and a much lower temperature is needed for lubricant desorption. In addition, we observed that hydrogen evolution from CHx overcoat initiates lubricant catalytic decomposition, forming CF3 and C2F5. The generation of HF during the thermal desorption experiments provides the formation mechanism of HF, which is the necessary component for catalytic reaction.

11:40am **AS+MI+VM-MoM11 Phase Transitions in Two-dimensional Ferroelectric Films***, **C.N. Borca**, J. Choi, S. Adenwalla, P.A. Dowben, M. Poulsen,* University of Nebraska, Lincoln*; J.L. Robertson,* Oak Ridge National Laboratory*; V.M. Fridkin, S.P. Palto, N. Petukhova, S.G. Yudin,* Russian Academy of Science*; S. Ducharme,* University of Nebraska, Lincoln

We studied ferroelctric copolymer films of vinylidene fluor ide with trifluoroethylene, P(VDF-TrFE) 70:30. The films exibit ferroelectric switching properties and can be used in a variety of piezoelectric devices. In addition to the first order ferroelectric to paraelectric bulk transition at 80 degrees C, we report two other phase transitions. One appears at 20 degrees C and is related entirely to a surface ferroelectric transition.@footnote 1@ The third transition around 150 degrees K is due to a stiffening of the lattice and a change in the bulk electronic structure. For P(VDF-TrFE), there is a negligible density of states at the Fermi level making this phonon related transition very unusual. This last transition was observed using neutron diffraction, @footnote 2@ X-ray diffraction, photoemission spectroscopy and EELS. The effective Debye temperature decreases from a value of about 250 K to 50 K with increasing temperature across the 150 K lattice stiffening transition. @FootnoteText@ @footnote 1@J. Choi, P.A. Dowben, S. Pebley, A.V. Bune, S. Ducharme, V.M. Fridkin, S.P. Palto, N. Petukhova, Phys. Rev. Lett. 80, 1328 (1998) @footnote 2@C.N. Borca, J. Choi, S. Adenwalla, Stephen Ducharme, P.A. Dowben, Lee Robertson, V.M. Fridkin, S.P. Palto, and N. Petukhova, Appl. Phys. Lett. 74, 347 (1999).

Applied Surface Science Division
Room 6A - Session AS-MoM

Imaging and Small Area Analysis

Moderator: J.E. Fulghum, Kent State University

8:20am **AS-MoM1 Reading Mechanism Evaluation on Detection of Spontaneous Polarization in a PZT Thin Film***, **W. Moon**,* Pohang University of Science and Technology, Republic of Korea*; H. Shin, J. Lee, K. Lee, Y.E. Pak,* Samsung Advanced Institute of Technology, Republic of Korea

The methods for detecting a small polarized area in a PZT thin film by SPM techniques are investigated theoretically and experimentally. A small polarized area in a PZT thin film can be constructed and detected by use of SPM. It is found that a 4 μ m by 4 μ m polarized area can be more easily detected by use of EFM techniques under contact-mode-AFM operation. It is shown experimentally as well as theoretically that effects of electrostatic forces are dominant for detection signals for polarized domains in a PZT thin film compared with piezoelectric vibration effects.

8:40am **AS-MoM2 A New Variable Temperature Beam-Deflection AFM***, A. Feltz, **P. Güthner**, T. Berghaus,* OMICRON Vakuumphysik GmbH, Germany

AFM experiments at variable temperature are very important for the investigation of phase transitions, growth behaviour, surface diffusion and other temperature depending processes on insulating surfaces with atomic resolution. For this purpose a new Variable Temperature AFM has been developed for minimum drift over a wide temperature range, i.e. AFM operation from 25 K to more than 1000 K. The special optical setup allows to realize a scanned-tip instrument. This allows to limit heating and cooling to the sample realizing a wide temperature range and low drift even for fast temperature changes. The beam deflection technique allows simultaneous topography and lateral force imaging in contact mode, non-contact mode AFM with true atomic resolution, as well as Magnetic Force Microscopy (MFM) and Electrostatic Force Microscopy (EFM). Au(111) was used to study friction at low temperatures. Images of the gold (111) surface in contact mode show the atomic structure and the 23 x @sr@3 surface reconstruction in the topography, and the friction image. At low temperatures down to 30 K the atomic scale friction is drastically increased. True atomic resolution has been achieved in dynamic mode images of silicon (111) 7x7 over a temperature range from 50 K up to about 1000 K. Silicon cantilevers prepared by sputter cleaning of the tip were used for these images. Further experiments will be performed on a non-conducting sample (NaCl).

9:00am **AS-MoM3 AFM Imaging of Thermal Phase Transitions in Polymers***, **S.N. Magonov**,* Digital Instruments **INVITED**

Atomic force microscopy (AFM) became the leading scanning probe technique, which is used in semiconductor, data storage, and plastics industries. AFM is routinely applied for examination of polymer materials at ambient conditions. Its validity for high-resolution real-space visualization of polymer morphology and nanostructure as well as for compositional mapping of heterogeneous systems had been already recognized. AFM substantially complements other microscopic and diffraction techniques providing visualization of single macromolecules and crystalline polymers, mapping of rubber domains with different cross-linking density and non-destructing imaging of sub-surface features of viscoelastic materials at depths from a few to hundreds of nanometers. Examination of structural changes at thermal transitions is a relatively new AFM capability. Several examples demonstrating such applications will be discussed in this contribution. They include monitoring of structural changes in mesomorphic polysiloxanes, thermal reorganization in block copolymers and visualization of melting and crystallization in ultrathin (20 nm) films of polyolefines.

9:40am **AS-MoM5 Geometry and Tip Effect Simulation in Scanning Kelvin Probe Microscopy***, **A.E. Efimov**,* Silicon-MDT Ltd., Russia*; S.R. Cohen, I. Visoly, D. Cahen,* Weizmann Institute of Science, Israel

Scanned probe microscopy (SPM) techniques have become an integral part of the fabrication and study of miniaturized devices, as well as of nm-scale features in general. Well-known geometric effects of tip size have been studied and several solutions were proposed for their removal from obtained topographical images. A more subtle effect exists for electronic surface mapping using such modes as scanning Kelvin probe microscopy (SKPM). These effects become significant for high resolution work on surfaces whose topography is not flat. We demonstrate this phenomenon on SKPM studies of CdTe films which exhibit both rich topography and electronic structure at grain boundaries. II-VI semiconductors exhibit interesting electronic properties which not only allow their applications in miniaturized electronic device structures, but suggests their study as model systems as an end in itself. A combined theoretical and computational approach is used to simulate the SKPM imaging process, calculate geometric contributions and separate electronic features from geometric distortions in the scanned probe images, in an attempt to recover the surface potential and therefore move towards true SKPM imaging. The results are compared with parallel techniques, such as scanning tunneling spectroscopy (STS), where the geometric contributions can be effectively ignored.

10:00am **AS-MoM6 Imaging of Particulates using Auger Electrons***, **M. Prutton**, D.K. Wilkinson, M.M. El Gomati, M. Jacka, M. Kirk,* University of York, UK **INVITED**

The currently favoured methodology of scanning Auger microscopy uses UHV SEM systems equipped with field electron emission sources in the column and coaxial mirror or concentric hemispherical electron energy analysers to detect electrons of a selectable kinetic energy. One technological objective is to produce digital maps in which the pixel intensities are proportional to the atomic fractions of the element giving that Auger line in the electron spectrum. This is significantly more difficult than simply acquiring and displaying signals proportional to the height or area of that Auger line because of the dependence of the Auger yield upon the local angle of incidence, the varying composition of sub-surface material and the presence of sharp changes in composition in the vicinity of the current pixel. Most of these difficulties have been removed or minimised in the York Auger microscope (MULSAM). The principal features of MULSAM will be outlined together with a short introduction to the methodology used to combine images obtained from several different scattered electron detectors around the sample. Examples will be given for correction of topographical artefacts in chemical maps and the use of multi-variate statistics to assist in the analysis of particulate catalysts. One disadvantage of current SAM designs is that sequential data acquisition is slow for multi-element samples. A new hyperbolic field analyser (HFA) will be reported that can acquire simultaneously an entire 1024 channel spectrum. It opens the way to obtain entire spectra in each pixel of an image. This could lead to very powerful methods of surface microanalysis using different parts of the spectrum in each pixel to correct for the local topographical and sub-surface composition. Some examples of spectra obtained from particulates using an HFA will be given. The outline design of a spectrum-imaging Auger microscope (SISAM) will be presented.

10:40am **AS-MoM8 Functionalised Plasma Polymer Coatings for Improved Durability of Aluminium-epoxy Adhesive Joints***, **B.J. Tielsch,*** Kratos Analytical, UK*; M.R. Alexander, G.E. Thompson,* The Corrosion and Protection Centre, UMIST, UK*; T.M. Duc,* BIOPHY Research S A, France*; E. McAlpine,* Alcan International, UK

There is much interest in the use of plasma polymer (PP) coatings to promote adhesion and/or inhibit corrosion of metals.@footnote 1@ These offer environmental and performance benefits over conventional "wet" processing methods such as chromic acid anodising (CAA). Here, we explore the use of carboxylic acid functionalised PP as an adhesion promotion coating on aluminium. The acid functionality, retained from the monomer structure in the plasma deposition process, is intended to form stable chemical bonds with both the aluminium oxide/hydroxide surface and epoxy based adhesives.@footnote 2@ Plasma polymerised acrylic acid and a plasma co-polymer of acrylic acid and octadiene, have been deposited onto plasma etched AA6016 aluminium alloy using RF deposition apparatus. An amine hardened epoxy-based adhesive formulation has been used to bond single lap shear (SLS) joints of PP-coated and CAA alloy. Combining tensile testing of SLS joints with locus-of-failure determination from imaging-XPS and TEM, the relative success of the pretreatments can be gauged. Joint durability was probed by testing joints after storage in water at 60 °C. A decrease in joint strength upon ageing was accompanied by a visual change from failure in the adhesive to failure at a near interfacial region. Chemical state differences in the XPS C1s core level between the acid containing PP and the epoxy containing resin were imaged over the fracture surface. This allowed the effect of PP deposition conditions upon the locus-of-failure and the relationship between this and the failure load to be investigated. Furthermore, information on the distribution of the amine hardener was obtained by imaging of the nitrogen peak. TEM examination of sections taken from the fracture surfaces was correlated with the information obtained using imaging XPS. @FootnoteText@ @footnote 1@R.H. Turner, I. Segall, F.J. Boerio, G.D. Davis, J. Adhesion 62, p. 1 (1997) @footnote 2@M.R. Alexander, S. Payan and T.M. Duc, SIA 26 p. 961 (1998).

11:00am **AS-MoM9 Glass Transition at Film Surfaces of Polymer Blends with Nanometer Spatial Resolution***, **F. Dinelli,*** University of Washington, US*; C. Buenviaje,* University of Washington*; M. Rafailovich,* State University of New York at Stony Brook*; R.M. Overney, R. Luginbuhl,* University of Washington*; J. Sokolov, X. Hu,* State University of New York at Stony Brook

Surface structure and properties of thin polymeric films are of crucial interest for many technological applications. In ultrathin polymer films we have found that interfacial interactions and local confinement alter the physical properties. Recently we have shown that the glass transition temperature at the surface of thin films can be accurately measured using shear modulation atomic force microscopy (AFM). In this paper we present a first application of this technique to polymer blends (PS/PBMA and PS/PMMA) which, depending on the film thickness and the local spinodal decomposition, offer quite complex folded interfacial regimes. In particular we will present profiles of the glass transition temperature across phase boundaries as a function of film thickness, relative composition and degree of mixing.

11:20am **AS-MoM10 Laser-SNMS and TOF-SIMS Characterization of Sub-µm Structures***, **R. Kamischke**, F. Kollmer, A. Schnieders, A. Benninghoven,* Universität Münster, 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 fine focused primary ion beam is applied. Whereas for molecular samples static SIMS is the technique of choice, element analysis can be achieved in addition by dynamic SIMS and by postionization of sputtered neutrals (SNMS). In sub-µm characterization the total amount of material available for an analysis is extremely small. Therefore the transformation probability of a surface atom into an ion should be optimized. The large fraction of sputtered neutrals and their efficient laser-postionization results in a high Laser-SNMS sensitivity. The use of a time-of-flight (TOF) mass spectrometer guarantees parallel mass registration at high transmission. In this contribution we report on recent results of TOF-SIMS and Laser-SNMS characterization of AFM tips (Si@sub 3@N@sub 4@ as well as Si after surface modification or metal loading, respectively) and of sub-µm particles, ranging in size down to 15 nm. The main intention of our investigations was to find out the limits in sensitivity for these two surface mass spectroscopies and to compare both techniques. All experiments were carried out in a gridless reflectron based time-of-flight instrument equipped with a fine focused Ga+ source (< 80 nm) and an excimer laser (248 and 193 nm) for nonresonant postionization. The instrument allows a direct comparison of SIMS and Laser-SNMS results of the same sample. We succeeded in chemical characterization of surface structures (nanotips as well as particles) down to the 10 nm scale by both techniques. Useful yields achieved in SIMS and Laser-SNMS reach 10@super -3@ and 10@super -2@, respectively. As a general result we found that the characterization of the elemental composition of structures with dimensions well below the spot size of the primary ion beam is possible.

Biomaterial Interfaces Group
Room 613/614 - Session BI-MoM

Biosensor-Biology Interface

Moderator: M.J. Tarlov, National Institute of Standards and Technology

8:20am **BI-MoM1 TOF-SIMS Investigation of the Immobilization Process of PNA and DNA Biosensor Chips***, **H.F. Arlinghaus**, C. Höppener, J. Drexler, M. Ostrop,* Physikalisches Institut der Universität Münster, Germany

A novel DNA sequencing method is described that uses peptide nucleic acid (PNA) hybridization biosensor chips. PNA is a synthesized DNA analog, in which both the phosphate and the deoxyribose of the DNA backbone are replaced by polyamides. This DNA analog retains the ability to hybridize with complementary DNA or RNA sequences. Because the backbone of DNA contains phosphates, of which PNA is free, an analysis technique that identifies the presence of phosphates in a molecular surface layer allows the use of unlabeled DNA for hybridization on a biosensor chip. We used TOF-SIMS to investigate its ability to distinguished between PNA and DNA molecules on surfaces, as well as the PNA and DNA immobilization process. For this purpose we immobilized silane SA-layers on UV/ozone treated silicon wafers and bonded PNA and DNA with different concentrations to these layers. It was found that the immobilization process is strongly dependent on the concentration and the immobilization time and that under optimized conditions, PNA and DNA can be covalently bonded to the silane SA-layers. A comparison between positive and negative TOF-SIMS spectra showed that the masses corresponding to PO@sub 2@@super -@, PO@sub 3@@super -@ and H@sub 2@PO@sub 4@@super -@ provide the best correlation to DNA presence. The phosphate yield could be significantly increased with polyatomic ion bombardment. Temperature-programmed SIMS (TP-SIMS) was used to measure the thermal stability of the immobilized layers showing that characteristic silane fragment ions decrease at a temperature of about 70°C. It can be concluded that the combination of TOF-SIMS and TP-SIMS provides a very useful technique for examining the complexity of the immobilization and hybridization processes of nucleic acid and that TOF-SIMS has the potential for providing a rapid method for DNA/RNA sequencing and diagnostics.

8:40am **BI-MoM2 Characterization and Quantitation of DNA on Gold***, **A.B. Steel,*** Gene Logic, Inc.*; R.L. Levicky,* Columbia University*; T.M. Herne, M.J. Tarlov,* National Institute of Standards and Technology

The interaction of DNA with gold has been characterized using a number of analytical techniques. The role of structural aspects of oligonucleotides, 8 to 48 nucleotide strands, on immobilization on gold has been investigated using electrochemistry, phosphorimaging, FT-IR spectroscopy, and neutron reflectivity. The value of incorporating a substrate-specific binding group was confirmed. In the case of binding to gold, the substrate-specific group is a thiol (SH). The packing density was studied as a function of the oligonucleotide length. The packing density is roughly constant for oligonucleotide segments less than 16 nucleotides in length. Longer strands pack on the surface at a density that is inversely proportional to the number of nucleotides in the segment. The data suggests that the conformation of single-stranded DNA transitions from a 'rigid rod' to a 'flexible coil' near this 16 nucleotide segment length.

9:00am **BI-MoM3 Gene Engineering for Biosensor-Biology Interface***, **M. Aizawa**, E. Kobatake, Y. Yanagida, T. Haruyama,* Tokyo Institute of Technology, Japan **INVITED**

Biosensor technology has made a remarkable progress in these three decades, which may be characterized by unique integration of immobilization and measurement technologies in the first generation, effective employment of advanced technologies such as microelectronics in the second generation and its own development based on generic technology in the third generation. Up to the second generation, the progress of biosensor technology has been realized by adopting the related technologies. It should be regretful, however, that no biosensor material, for instance, has been designed or synthesized for its own purpose. Much effort has been devoted to adopting a native biomolecule to fit a biosensor. It is not until the third generation that biosensor material is designed for its own purpose on the basis of advanced technology. For the progress of biosensor technology, sensing material design technology should be advanced in harmonization with process technology as well as system technology. As far as sensing material design technology, we should concentrate on designing biosensing materials on the basis of gene engineering for the development of the third generation of biosensors. Gene engineering may fall in three categories of engineering including gene designing of proteins, designing of gene expression process and gene diagnosis. In this paper, both gene designing of proteins and designing of gene expression processes for biosensing are described with focusing on our current achievement.

9:40am **BI-MoM5 Cell-Transistor Coupling***, **A. Offenhäusser**,* Max-Planck Institute for Polymer Research, Germany

In recent years it became conceptually feasible to study small networks of synaptically interactive neurons in vitro. Input (stimulation of a single neuron) and output (recording of electrical signals from individual neurons) control in such a neural network could be achieved by direct coupling of the neural electrical signals to a field-effect transistor (FET) device and metal microelectrodes, opening up the possibility for two-way, nontoxic communication between chips and nerve cells. However, the cell-device coupling is not very well understood and the control of this coupling challenging. An extracellular recording system has been designed for the detection of electrical cell signals.@footnote 1@ A field-effect transistor (FET)@footnote 2@ array has been fabricated which consists of p-channel or n-channel FETs with non-metallized gates. The size of the gates of the 16 FETs are from 16x3 um2 down to 5x1 um2 and are arranged in a 4x4 matrix on 200 and 100 um centers. On the other side extended gate electrode (EGE) arrays were used which are arranged in a 8x8 matrix on 200 and 100 um centers. The gate electrodes are made from gold, titanium and silicides with diameters down to 6 um. The cell-device coupling has been studied using various cell types e.g. neuronal cells, cardiac myocytes, and cells from cell lines. The recorded signals will be discussed on the base of a point contact model where contributions from passive as well as active membrane properties are included. @FootnoteText@ @footnote 1@ C. Sprössler, D. Richter, M. Denyer, A. Offenhäusser, Biosens.& Bioelec. 13, 613-618 (1998). @footnote 2@ A. Offenhäusser, C. Sprössler, M. Matsuzawa, W. Knoll, Biosens.&Bioelec. 12, 819-826 (1997).

10:00am **BI-MoM6 Specific Interactions between Bitoin and Avidin Studied by AFM using the Poisson Statistical Analysis Method***, **T.P. Beebe**, Y.-S. Lo, N.D. Huefner, W.S. Chan, B.A. Shiley, F. Stevens,* University of Utah

The interactions between biotin and avidin or streptavidin, a prototypical example of specific biological ligand-receptor systems, were studied by atomic force microscopy (AFM). A unique statistical analysis method which makes use of the properties of the Poisson distribution was applied, and the rupture strength of an individual interaction was obtained from the total pull-off forces measured by the AFM. Tip- and surface-modification chemistries were investigated by X-ray photoelectron spectroscopy (XPS) and time-of-flight secondary ion mass spectrometry (TOF-SIMS). The Poisson analysis method has several advantages. It requires no assumptions about the surface energies or contact area between the AFM tip and the substrate, it is not limited by the force resolution of the instrument, and the number of measurements required to extract the individual unbinding force is significantly lower than that required by some other methods. It has been shown that bond rupture strengths are dependent on the rate and duration of force loading applied during the unbinding process. The dynamic nature of bond strengths under external forces has been explored in theory and by several computer simulations, however, only very few experimental studies have been reported. In the present study, we measure the unbinding force of the biotin-streptavidin pairs under various loading rates. The loading rate dependence of bond rupture forces and the comparison of our experimental data to the known thermodynamic properties of the system will be discussed.

10:20am **BI-MoM7 Manipulation of Cellular Interactions with Biomaterials toward aTherapeutic Outcome***, **M.D. Pierschbacher**,* Integra LifeSciences Corporation **INVITED**

A new way of manipulating the manner in which cells interact with biomaterials was made possible with the discovery of arginine-glycine-aspartic acid (RGD) as a major cell recognition signal in the extracellular matrix. This RGD signal has been incorporated into synthetic compounds that can function as antagonist or agonist for a class of cell surface receptors called integrins. In the agonist mode, these compounds can be coupled or bound to wide variety of biomaterials to present a target for the physiological interaction of cells with the surface of these materials through one or more of the integrin types expressed on the cell surface. The agonist activity of these compounds is evident from an in vivo response of faster and more complete tissue integration and a reduction in foreign body response. There are more than 25 different integrin subtypes, and different cell types express a unique subset of these on their surface. More than half of the integrins recognize and bind to a form of the RGD signal in their natural ligand and can distinguish one form of RGD from another. Specific tissue responses such as vascualization or mineralization can be achieved by immobilizing compounds with the appropriate integrin specificity.

11:00am **BI-MoM9 Investigations into Peptide-tethered Lipid Bilayer Membranes***, **L.C.R. Naumann**,* Max-Planck Institute for Polymer Research, Germany*; E.K. Schmidt,* Institute of Physical and Chemical Research (RIKEN), Japan*; A. Offenhäusser, W. Knoll,* Max-Planck Institute for Polymer Research, Germany

Lipid-functionalised thiopeptides were employed to form peptide-tethered lipid monolayers on gold substrates. Upon fusion of liposomes these monolayers formed tethered lipid bilayer membranes (tBLM's) well designed to incorporate membrane proteins such as H+-ATPase, Na,K-ATPase, cytochrome c oxidase (COX) and the acetylcholine receptor (AChR). Pure peptide-tBLMs and those mixed with a lateral spacer such as thioethanol were investigated with regard to protein incorporation which was followed by surface plasmon resonance spectroscopy (SPS). Electrical properties were assessed simultaneously by impedance spectroscopy (IS). Fluorescence microscopy showed the bilayers to be homogeneous, however, by FRAP measurements fluidity of the membranes was not observed. Fluorescence microscopy was also used to determine the surface concentration of fluorescein labeled COX. Binding assays were performed by SPS of agonists and antagonists of the receptors such as cyochrome c and bungarotoxin. The specificity and sensitivity of the binding assays was increased for primary monoclonal and secondary polyclonal antibodies against COX and the AChR by using an extension of SPS, surface plasmon enhanced fluorescence spectroscopy (SPFS). Proton transport through H+-ATPase from chloroplasts was then investigated with either coupled or non-coupled proton discharge at the gold electrode, depending on the applied potential. In cases where faradaic processes were involved, electrochemical techniques were applied, such as square wave voltammetry and chronoamperometry, where as proton transport across the lipid film was followed by IS. Impedance spectra thus showed characteristic changes as a function of adenosin-triphosphate (ATP) and inhibitor (venturicidin) concentration and/or bias potentials.

11:20am **BI-MoM10 Detection of Immobilized Superparamagnetic Nanosphere Assay Labels using Giant Magnetoresistive Sensors***, **M.C. Tondra**,* Nonvolatile Electronics*; M. Porter,* Iowa State University

Commercially available superparamagnetic nanospheres are commonly used in a wide range of biological applications, particularly in magnetically assisted separations. A new and potentially significant technology involves the use of these particles as labels in nanomagnetic assay applications. This labeling is analogous to that of flourescent beads: the beads are excited and detected with magnetic fields rather than with photons. A major advantage of this technique is that the means for label excitation and detection are easily integrable on a silicon circuit. A preliminary study of this technique demonstrated its basic feasibility, and projected a sensitivity of better than 10@super -12@ Mole.@footnote 1@ This paper presents detailed magnetic and geometric design considerations for this type of assay, and addresses the range of applications over which the technique is appropriate. It is shown that, with proper sensor design and immobilization techniques, integrated magnetoresistive sensors can be used to easily detect the presence or absence of single 1000 nm magnetic microspheres immobilized on the surface of a giant magnetoresistive sensor. Detection of microsphere labels in the 10 to 100 nm range may also be possible if other sensing parameters are compatible. @FootnoteText@ @Footnote 1@ David R. Baselt, Gil U. Lee, Mohan Natesan, Steven W. Metzger, Paul E. Sheehan, and Richard J. Colton, "A Biosensor Based on Magnetoresistance Technology," Biosensors and Bioelectronics, Vol. 13, pp. 731-739 (1998).

11:40am **BI-MoM11 Characterization of S-layer-supported Bilayer Lipid Membranes*, B. Schuster*,** *D. Pum, U.B. Sleytr,* Universität für Bodenkultur Wien, Austria

Biosensors, based on electrical detection of specific ligand binding become of increasing importance over the last years. Reliable application make great demands on these designed systems like stable membranes with sufficient fluidity and controlled, orientated linkage of sensing molecules to benefit from the various biological interactions. One promising strategy is the application of bacterial-cell-surface-layers (S-layers) as biocompatible and supporting structures for bilayer lipid membranes (BLM's). S-layer are the simplest self-assembly systems that produce crystalline, mono-molecular, isoporous protein lattices with well-defined topographical and physico-chemical properties. Recent studies on S-layer-supported BLM's demonstrated, that the fluidity of the BLM is retained and an enhanced stability is observed as these BLM's reveal a decreased tendency to rupture in the presence of ionophores or pore-forming proteins. Furthermore, S-layer proteins can be recrystallized on solid supports like gold or silicon wafers, and provide a biocompatible, water-containing layer. Attached BLM's exhibit an increased fluidity compared to dextran- or silane-supported BLM's and the stability is significantly enhanced. Thus, S-layer can be used as an alternative to soft polymer cushions and to common tethers to support functional BLM's. Additionally, a second S-layer can be recrystallized on the opposite face of the membrane. This will allow to employ the intrinsic molecular sieving properties and to immobilize a range of biologically functional molecules in a well-defined position and orientation on the S-layer lattice. Thus, BLM's with attached S-layer(s) in combination with new sensor technology might play an important role in the development of biosensors.

Electronic Materials and Processing Division
Room 608 - Session EM-MoM

Nitride Epitaxy

Moderator: M.R. Melloch, Purdue University

8:20am **EM-MoM1 GaN Growth Chemistry, System Design and Materials Properties*, T.F. Kuech*,** *J. Sun, L. Zhang,* University of Wisconsin, Madison*; J.M. Redwing,* Epitronics **INVITED**

The growth of device-quality GaN by metal-organic vapor phase epitaxy (MOVPE) is often difficult to achieve. The MOVPE growth of GaN is complicated by the extensive and pervasive complex gas phase chemistry within the growth system. This gas phase chemistry leads to the high sensitivity of the materials properties on the detailed fluid dynamics within the system. Through the combination of reactor modeling and gas phase kinetic studies, we have identified a stratified gas phase chemical structure within the reactor that leads to such process complexities. The high gas phase flow rates employed in GaN MOVPE results in a very thin high-temperature gas flow region above the growth front that leads to extremely high thermal gradients. Inside this thin high-temperature flow region, dominant chemical species above the growth surface changes in the gas phase above the growth front as a result of the high thermal gradient present and the high molecular weight species resulting from the oligimerization of the adduct. This chemically stratified region is closely related to the transport and reaction behavior present in GaN MOVPE processes and the modeling of this near-growth-front region serves as an engineering guideline for GaN MOVPE reactor design. We have combined these numerical results with detailed experimental measurements within the modeled system. The implications of these findings for the design of GaN systems and materials performance will be discussed. The extension of these models to the case of selective are growth of GaN will be discussed in terms of the local gas phase activities of the reactants and their influence on the facet formation.

9:00am **EM-MoM3 Mechanisms for Lateral Growth and Coalescence in GaN CVD*, M.E. Bartram*,** *M.E. Coltrin, J. Han, C.C. Willan,* Sandia National Laboratories

Recent observations of rapid coalescence occurring upon convergence of lateral growth fronts suggest new strategies for GaN selective area growth (SAG) techniques. A mask with systematically spaced nucleation zones was used to provide a pseudo time-base for observing lateral growth transitions within a single GaN deposition. Scanning electron microscopy (SEM) revealed that the joining of adjacent features initiated a secondary lateral growth mechanism. The profile of the coalescence region suggests this rapid mode of deposition was controlled by layer-by-layer growth in which each new growth surface defined a reactive step against the initial growth front for nucleation of the next layer. This buildup thus driven by the lateral rate, resulted in the vertical growth front in the coalescence region meeting the upper most surface of the initial growth features. The layer-by-layer coalescence mechanism was quite independent of the slower progress of the original growth fronts when the V/III ratio was sufficiently high. However, it was non-existent under low V/III conditions. Correlations with materials quality will be made using TEM and CL measurements.

9:20am **EM-MoM4 Selective Area Growth of GaN on Si by Chemical Beam Epitaxy**, *E. Kim,* ***A. Tempez****, N. Medelci, I.E. Berishev, A. Bensaoula,* University of Houston

One possible advantage of high vacuum deposition techniques over MOCVD is the realization of GaN device structures on Si wafers. In the case of MOCVD and sapphire substrates, selective GaN lateral regrowth over SiO@sub 2@ masks has been shown to reduce considerably the defect density in the epilayers. Thus far, very little data is available for regrowth using MBE techniques. In our previous studies of GaN deposition by chemical beam epitaxy (CBE) with TEGa and ammonia precursors, we have shown that no nucleation occurs on a sapphire surface. Using the same CBE precursors, we investigate here the selective nucleation process on Si wafers patterned with various oxide and nitride masks. The selectivity of the nucleation process was monitored in real time using time of flight ion scattering and recoil spectroscopy and RHEED. Two direct recoil spectroscopy (DRS) detectors mounted at 40 and 70° recoil angles are associated with MSRI (mass spectroscopy of recoiled ions) analyzers (sector and reflectron, respectively). These time refocusing analyzers allow for higher resolution and sensitivity than DRS. Our results show that the MSRI Si to O peak intensity ratio during GaN regrowth of SiO@sub 2@ patterned GaN is constant within the condition range we explored. This shows a 100% selective overgrowth process and is confirmed by SEM analysis. Following these experiments, we then implemented various regrowth schemes such as the use of a thin AlN single crystal layer on Si by a reactive MBE method followed by patterning and etching in an Ar-Cl@sub 2@-BCl@sub 3@ RF plasma. In this presentation, we will summarize our observations on the effect of the growth conditions (growth temperature and Ga/N flux ratio) on the selectivity of the nucleation process and will show our most recent data on the optimized regrown GaN layers- including their optical, electrical and field emission properties.

9:40am **EM-MoM5 The Role of Extended Defects in the Physical Properties of GaN and its Alloys*, J.S. Speck*,** University of California, Santa Barbara **INVITED**

GaN and its alloys have emerged as the leading wide bandgap materials system for electronics and optoelectronics applications despite the high extended defect densities encountered in state-of-the-art device material. Pure edge character ('a' Burgers vector) or mixed character ('a+c' Burgers vector) threading dislocations with densities in the mid-108 to 1010 level are the predominant extended defects in high quality MOCVD-grown GaN on sapphire or silicon carbide substrates. We review the origin of these along with other extended defects (e.g., stacking disorder and inversion domains) and relate the growth to basic capillary-governed growth phenomena. Recently, a new technique, lateral epitaxial overgrowth (LEO), has emerged as a technique to reduce the density of extended defects by 3 - 4 orders of magnitude. The basic growth processes and extended defect evolution in LEO growth will be presented LEO GaN can also be used to directly compare the physical properties of dislocation-free and dislocated GaN. We show in experiments on LEO and 'normal' (bulk) GaN that threading dislocations behave as charged scattering centers, non-radiative recombination centers, and current leakage paths. Additionally, threading dislocations are the most common origin of deviations from planar growth and lead to a variety of kinetically-limited growth morphologies. Finally, highlights of some of our recent work on MBE growth of GaN will be presented, including record mobilities for 2-dimensional electron gas in AlGaN/GaN heterostructures.

10:20am **EM-MoM7 Growth Kinetics of GaN(0001) as Grown by MBE@footnote1@*, A. Parkhomovsky,*** *S.M. Seutter, B.E. Ishaug, A.M. Dabiran, P.I. Cohen,* University of Minnesota*; S. Keller, S.P. DenBaars,* University of California, Santa Barbara

The kinetics of growth of GaN films using molecular beam epitaxy with a Ga K-cell and an NH@sub 3@ leak was studied. GaN(0001) layers grown by metalorganic chemical vapor deposition on c-plane sapphire were used as substrates. In situ growth monitoring was conducted using reflection high energy electron diffraction (RHEED) and desorption mass spectroscopy (DMS). The films were characterized in situ by UHV scanning tunneling microscopy (STM) and ex situ by atomic force microscopy. Prior to the growth the substrates exhibited a 2D RHEED pattern characteristic of a smooth surface with atomic steps. Initial growth of GaN under Ga rich conditions on this surface at 760°C produced a rough surface as indicated by a 3D RHEED pattern. We suggest that the roughening is due to a surface contamination that changes the growth kinetics, causing faceting of the surface. The surface was then gradually smoothened by growing under the same excess Ga conditions. On a smooth surface, RHEED intensity oscillations were observed for both the excess Ga and excess NH@sub 3@ growth regimes. This is very different from the GaN(000-1). Like the GaN(000-1), the RHEED oscillations were observed in the excess NH@sub 3@ regime at Ga beam equivalent pressures ranging from 3x10@super-7@ to 5x10@super-7@ Torr and an ammonia BEP from 0.5x10@super-4@ Torr to 1.0x10@super-4@ Torr at a substrate temperature of 600°C. Unlike GaN(000-1), the RHEED oscillations were seen in the excess Ga regime at a Ga BEP of 1.4x10@super-6@ Torr, NH@sub 3@ BEP of 1.6x10@super-7@ Torr and at a substrate temperature of 760°C. Upon initiation of the Ga flux, DMS measurements indicated a single step increase in the Ga desorption signal which is different from the two-step increase on the GaN(000-1) associated with a physisorbed state. UHV STM studies were conducted on fully gallided and partially nitrided quenched GaN surfaces. Partial nitridation of GaN(0001) surface in ammonia produced nitrided zones at step edges that are 15-20 nm in size and 2-3 ML deep. The size of the zones is much less than that on the GaN(000-1) surface. @FootnoteText@ @footnote1@ Partially supported by the Office of Naval Reasearch and the National Science Foundation

10:40am **EM-MoM8 Dissociation of Al@sub 2@O@sub 3@(0001) Substrates, and the Roles of Silicon, Oxygen, and Nitrogen Vacancies in n-type GaN Grown by MBE*, J.E. Van Nostrand,*** Air Force Research Lab*; J.S. Solomon,* University of Dayton Research Institute*; A. Saxler,* Air Force Research Lab

GaN is a semiconductor material that shows great promise for use in optoelectronic and electronic devices due to its large, direct bandgap. However, in spite of astonishing and rapid developmental successes, many problems remain that hinder further progress. Among them is a lack of understanding of the mechanisms underlying impurity incorporation, the nature of native defects, and the dependence of both of these on the thermodynamics and kinetic limitations of the GaN growth technique employed. One nearly universal aspect of unintentionally doped GaN films grown on sapphire by any technique is an n-type background carrier concentration. This phenomenon has been attributed to impurities such as Si or O, or to native defects such as N vacancies. In this work, we identify and quantify an anomalous relationship between the Si doping concentration and free carrier concentration and mobility using temperature dependent Hall measurements on a series of 2.0 µm thick GaN(0001) films grown on sapphire with various Si doping concentrations. Secondary ion mass spectrometry (SIMS) is used to identify the type of the excess free carriers to be oxygen. Further, the source of the oxygen is positively identified to be dissociation of the sapphire substrate at the sapphire-nitride interface. Finally, SIMS is again utilized to show how Si doping can be utilized to control the diffusion kinetics of the oxygen into the GaN layer from the sapphire substrate.

11:00am **EM-MoM9 Growth of GaN Thin Films and Device Structures on Silicon Wafers by Molecular Beam Epitaxy*, I.E. Berishev,*** *D. Starikov, N. Medelci, A. Bensaoula, I. Rusakova, E. Kim,* University of Houston

GaN grown on Si wafers has large perspectives in various device applications due to low cost of the substrate and easy integration with well developed Si circuits. More over, molecular beam epitaxy is advantageous in this respect due to low growth temperature and advanced methods of in situ characterization. We report the growth of GaN - based heterostructures and light emitting devices on Si (111) wafers by molecular beam epitaxy with a RF nitrogen plasma source. We found that the buffer layer between the Si and the GaN epilayer is the most critical factor responsible for the properties of the active device layers. To that end, several buffer layers, including AlN, GaN and Si-@sub x@N@sub y@ were studied in situ by RHEED and time of flight mass spectroscopy of recoiled ions and ex situ by transmission electron microscopy. Inter-diffusion between Si and Al(Ga) was studied by SIMS. We found that diffusion of group III elements into the substrate is much stronger than diffusion of Si into the upper layers. Optimized growth conditions for the buffer layer, the thick GaN layer, and p-type GaN layer allowed for injection light emitters to be fabricated. Ternary alloys, including InGaN quantum well active regions, are currently under development. Our most recent data on X-ray diffraction, photo-luminescence and electro-luminescence of fabricated light emitting diodes on Si (111) wafers will be presented at the conference.

11:20am **EM-MoM10 Photoluminescence and Heteroepitaxy of ZnO on Sapphire Substrate (0001) Grown by RF Magnetron Sputtering*, K.K. Kim,*** *S.J. Park,* Kwangju Institute of Science and Technology, Korea*; J.-H. Song,* Korea Institute of Science and Technology, Korea*; H.-J. Jung, W.K. Choi,* Korea Institute of Science and Technology, Seoul

ZnO thin films were epitaxially grown on Al@sub 2@O@sub 3@ (0001) single crystalline substrate by RF magnetron sputtering with the variations of RF power P=60-120 W. Crystalline structure of the ZnO films were analyzed by 4-circle X-ray diffraction, backscattering (BS)/channeling, and transmission electron microscopy. At the substrate temperature 550@super o@C, the ZnO film deposited with power of 80W has narrowest full width half maximum(FWHM) of @theta@-rocking curve, 0.16@super o@, indicating an highly c-axis oriented columnar structure. XRD @theta@-rocking curve FWHM of the ZnO film deposited at 120 W and 600@super o@C was 0.13@super o@ and in-plane of ZnO grown on sapphire(0001) substrate was found to be indicated a 30@super o@ rotation of ZnO unit cell about sapphire(0001) substrate. In BS/channeling study, channeling yield minimum (@chi@ @sub m@) was changed with growing temperature and power, and was only 4-5% for the films deposited at 120 W, 600@super o@C. In PL measurement, only the sharp near band edge (NBE) emission were observed at room temperature for the films deposited at 80-120 W and 550@super o@C and 120 W, 600@super o@C. but deep-level emission were also detected in the films deposited at 60 W, 550@super o@C. The FWHM was decreased from 133 meV to 89 meV as RF power increased from 80 W to 120 W at 550@super o@C, and that of film deposited at 120 W and 600@super o@C showed 76 meV which is lower value than any other ever reported, which were somewhat opposite to that of XRD. From TEM analysis, grain size and defect were found to affect the PL properties. In this study, the PL property of undoped ZnO thin films is discussed in terms of the crystalline structure and the quality of grain.

11:40am **EM-MoM11 Characterization of a Very Thin Film: N2 Plasma Nitridation of GaAs (110)*, J.E. Hulse,*** National Research Council of Canada, Canada*; D. Landheer, R. Krishnamurthy, S. Moisa,* National Research Council of Canada

GaAs (110) wafers were prepared by cycles of UV-ozone/HF cleaning and inserted into an Ultra-High Vacuum processing system. Nitridation of the wafers by a remote Electron Cyclotron Resonance (ECR) nitrogen plasma produced a porous GaN film of up to about 3 nm in thickness. In situ analysis by X-ray Photoelectron Spectroscopy (XPS) revealed that the plasma both scoured the GaAs substrate surface of carbon and oxygen and produced a GaN film. Ex situ analysis by Spectroscopic Ellipsometry indicated that the GaN layer was porous. Angle-Dependent XPS demonstrated that the GaN layer contained traces of As predominantly in the outer regions of the film, and that the porous GaN can absorb water on exposure to air. A 5 second exposure of a GaAs (110) wafer to the ECR nitrogen plasma simulates the initial stage of ECR plasma deposition of silicon nitride, which exposes the substrate to a nitrogen plasma at turn-on. Such a short nitridation produced a GaN film that was 1.9 nm thick with traces of arsenic throughout and approximately 50 % voids. Longer exposures to the nitrogen plasma produced films whose thicknesses followed an inverse power law time dependence. The wafers were examined by Atomic Force Microscopy both before and after nitridation. Before plasma nitridation, the cleaned wafers showed clearly identifiable roughness features due to chemical-mechanical polishing. Plasma nitridation left the surface smooth and free of identifiable features less than 10 microns in lateral size.

Flat Panel Displays Topical Conference
Room 604 - Session FP+VT-MoM

Field Emission Displays and Vacuum Packaging Issues

Moderator: W. Weed, Sandia National Laboratories

8:20am **FP+VT-MoM1 A New Field Emission Device with Improved Vacuum Features***, **V.P. Mammana**,* Instituto de Física - Universidade de São Paulo, Brazil*; F.T. Degasperi,* Faculdade de Tecnologia de São Paulo - FATEC/SP, Brazil*; O.R. Monteiro,* Lawrence Berkeley Laboratory*; J.H. Vuolo, M.C. Salvadori,* Instituto de Física - Universidade de São Paulo, Brazil*; I.G. Brown,* Lawrence Berkeley Laboratory

We introduce in this article a novel geometry that can be used in the manufacturing of field emission displays that combines superior vacuum conductance and field enhancement factors. A theoretical model is developed for the calculation of the upper limit of the electrostatic field at the emitting regions, and these values are compared to those calculated for the actual geometry. The vacuum conductance of the proposed geometry is also calculated, and we show that conductances up to an order of magnitude higher than other schemes are readily achievable.

8:40am **FP+VT-MoM2 Fabrication of a Well-Type Field Emission Device with a Tungsten Doped Zinc Oxide Thin Film Phosphor***, **V. Bhatia**, J.B. Sobti, L.D. Karpov, M.H. Weichold,* Texas A&M University

Interest in the area of the field emission displays (FEDs) exists because of combination of the positive features of a cathode ray tube with flat panel display technologies. High resolution at low cost, power efficiency at low voltage operations, wide viewing angles, and operation under variable temperatures are some of the important features of an FED. This paper reports the fabrication of a monochromatic display of blue light from a lateral edge well emitter. A high-resolution display has been fabricated using a blue phosphor developed at TAMU@footnote 1@ in conjunction with a well type edge field emission device designed by Karpov et al.@footnote 2@ The FED has been formed by constructing arrays of wells, having sides of a dielectric material above a matrix of anode lines. The anode lines lie underneath the phosphor. In the diode design of the device, cathode lines are fabricated by depositing metal-carbon-metal layers, atop the well sides, hanging slightly over the well edges. The FED design reported here provides an extra measure of brightness to the display by reflecting the light from anode lines out of well towards the viewer. Since the device eliminates the fabrication of microtips, the display involves simpler fabrication steps, more ruggedness, and stability than conventional FEDs. The phosphor being used in this display, has been fabricated by co-depositing zinc oxide and tungsten (ZnO:W). This phosphor has been reported to emit blue light at 490 nm when excited at 300 V.@footnote 3@ This paper presents ongoing research in integrating the ZnO:W phosphor in the well type edge field emission display. The fabrication steps involved in making the display device are presented as are emission properties and current-voltage characteristics to determine the performance of the display. @FootnoteText@ @footnote 1@Technology Disclosure to TAMU Technical Licensing Office (1993). @footnote 2@L. D. Kapov et al. 7th Int'l Vacuum Microelectronics Conf., France 1994. @footnote 3@J. B. Sobti et al. MRS meeting, Spring 1998.

9:00am **FP+VT-MoM3 Effects of Residual Gas Exposures on the Emission Characteristics of Field Emission Arrays***, **R.M. Wallace**, B.E. Gnade,* University of North Texas*; B.R. Chalamala,* Motorola Flat Panel Display Division **INVITED**

Field emitter arrays have been introduced as a potential component for flat panel display technologies. A key issue for reliable performance includes the consideration of the device vacuum ambient in the course of packaging the display. In this paper, we review the effects of residual gas species on the emission characteristics of field emitter arrays under carefully controlled UHV conditions. We also examine recent work in the community on controlling the tip morphology, the tip surface chemistry, and the sources of residual gas species in displays.

9:40am **FP+VT-MoM5 Pressure Field Detailed Calculations for a New Field Emission Device with Improved Vacuum Features@footnote 1@***, **F.T. Degasperi**,* Faculdade de Tecnologia de São Paulo - FATEC/SP - Brazil*; V.P. Mammana,* Instituto de Física da Universidade de São Paulo, Brazil

The vacuum characteristics are an important consideration for field emission devices, mainly because of the high area/volume ratio presented in these devices. Dessorption associated with relatively small conductances can degrade the device performance over its lifetime, if small distances between the cathode and the anode are set. The proposal of a novel geometry for these devices@footnote 1@ seeks superior vacuum conductance, while maintaining a high electric field enhancement factor. It is of great importance to determine the pressure distribution along the emission chamber of the proposed device, since the emission performance is strongly dependent on this pressure. The usual vacuum technology approach considers a vacuum system made up of discrete elements. This approach is very useful, but leads only to the knowledge of the average pressure, and not to the detailed pressure distribution. In this article we calculate the pressure distribution considering the degaseification effect from several surfaces of the device, which allows us to predict its vacuum behaviour in a more realistic situation. @FootnoteText@ @footnote 1@ see "A new field emission device with improved vacuum features".

10:00am **FP+VT-MoM6 Cathodoluminescent (CL) Degradation Mechanism for ZnS-Based Phosphors and the Impact on Field Emission Displays (FEDs)***, **B.L. Abrams**, W. Roos,* University of Florida*; H.C. Swart,* University of the Orange Free State*; P.H. Holloway,* University of Florida

The surfaces of ZnS powder and thin film phosphors have been subjected to electron beam bombardment.Simultaneous acquisition of CL brightness data and Auger Electron Spectroscopy(AES)data have revealed a correlation between surface chemical reactions and CL degradation.The data were collected in a stainless steel UHV chamber.In the presence of a 2kV primary electron beam in 1e-6 Torr of H2O,the amounts of C and S on the surface decreased while the O concentration increased.XPS data showed that ZnO formed on both the samples.This change in surface chemistry coincided with a decrease in CL brightness.Our model of electron beam stimulated surface chemical reactions(ESSCR)for this degradation process postulates that the primary electrons dissociate physisorbed molecules to reactive atomic species. These atomic species remove surface S and C as volatile SOx and H2S species allowing formation of a non-luminescent ZnO layer in 1e-6 Torr water.However,in a vacuum of 1e-6 Torr dominated by hydrogen and with a low water content, there was no decline in S,no rise in O,but the CL still degraded.These effects are still attributed to ESSCR due to hydrogen assisted by thermal effects.Hydrogen is postulated to dissociate under the electron beam and remove S as H2S while Zn volatilizes due to a high vapor pressure and elevated temperatures from electron beam heating.The desorption of various ions or molecules from the surface of the phosphor caused by surface chemical reactions contaminate the vacuum inside the display tube and create a reactive environment.These reactive atoms or molecules may adsorb,react and consequently form an absorbed or coated layer(sulfide or oxide)on the field emitter tip on the cathode side of the FED.It is thus suggested that the ESSCR mechanism is important to degradation both of the phosphor on the anode and the field emitter tips on the cathode.This work was supported by Darpa Grant MDA 972-93-1-003 through the Phosphor Technology Center of Excellence.

10:20am **FP+VT-MoM7 A Novel Electron Emission Flat Panel Display Using Cesiated Amorphous Diamond Planar Emitter Structure***, **S. Kim**, M.H. Sohn, Y.S. Park, N.W. Paik, B. Lee,* SKION Corporation*; Y.H. Lee,* Sung-Kyun-Kwan University, S.Korea, Korea*; D.H. Lee, Y.J. Sung,* Sung-Kyun-Kwan University, S.Korea*; G.Y. Yeom,* Sung-Kyun-Kwan University, S.Korea, Korea

Oxidized cesiated amorphous diamond films have been developed for electron emitters. The work function of the surface is as low as 1.05 eV. The work function, chemical composition and structure are found to be stable even after annealing at temperatures up to 700 degree C. A very low turn-on field of 5-7 V/μmm is obtained by a planar geometry field emission measurement. A unique Pierce-type planar electron extraction geometry has been developed for flat panel display applications. Unlike field emission from a sharp point, the structure produces a long focal length beam of the order of few centimeters. In this paper, the fabrication procedure of the emitter structure and its emission properties will be presented.

10:40am **FP+VT-MoM8 Field Emission Properties of Conformal and Non-Conformal Diamond Film Coatings on Si Microtip Electron Emitters***, M.Q. Ding,* Beijing Vacuum Electronics Research Institute, China*; **A.R. Krauss**, O. Auciello, D.M. Gruen, Y. Huang,* Argonne National Laboratory*; V.V. Zhirnov,* Semiconductor Research Corp.*; E.I. Givargizov, A. Stepanov,* Institute of Crystallography, Russia

Non-conformal and conformal nanocrystalline diamond films were deposited on single needle-shaped Si tip emitters, using hot filament chemical vapor deposition (HFCVD) and microwave plasma-enhanced chemical vapor deposition (MPECVD), respectively. The HFCVD diamond was deposited in the form of large single crystal grains at the end of the microtips, whereas the nanocrystalline diamond films were uniformly thick conformal coatings. The threshold voltages for cold cathode electron emission were measured for Si microtips as a function of both the thickness of the diamond coating and the radius of the Si tips. The threshold voltages for the single crystal HFCVD coatings were found to vary with both the tip radius and diamond film thickness. For the nanocrystalline films, the threshold fields were found to be significantly lower than the uncoated tips, and nearly independent of both Si tip radius and film thickness. In this case, the behavior is consistent with field emission that is determined largely by local electric field enhancement associated with intrinsic film properties. A model is presented in which the field enhancement occurs at sp2-bonded grain boundaries. Work supported by the U.S. Department of Energy, BES-Materials Sciences, under Contract W-31-109-ENG-38, and ER-LTR CRADA No. C9501501 with SI Diamond Technology, Inc., Austin, TX, and DARPA/ONR under Contract N00014-97-F0305 The submitted manuscript has been created by the University of Chicago as operator of Argonne National Laboratory under contract no. W-31-109-ENG-38 with the U. S. Department of Energy. The U. S. Government retains for itself, and others acting on its behalf, a paid-up, non-exclusive, irrevocable worldwide license in said article to reproduce, prepare derivative works, distribute copies to the public, and perform publicly and display publicly, by or on behalf of the government.

11:00am **FP+VT-MoM9 Fabrication of Aligned High-density Diamond Needles by Dry Etching of Diamond Substrates***, E.S. Baik,* Myong Ji University, Korea*; Y.J. Baik,* Korea Institute of Science and Technology, Korea*; **D. Jeon**,* Myong Ji University, Korea

Densely packed diamond needles aligned in the same direction are formed by air plasma etching of diamond substrates. Diamond substrates were coated with a thin layer of Mo and then etched by RF or DC plasma with the substrate biased at negative several hundred volts. The shape and the density of the diamond needles could be reproducibly controlled with the etching parameters such as the substrate temperature, pressure, bias voltage, power, and the amount of Mo. If the substrate temperature was high, for example, the needles became thick. Mo acted as an etch-resistant mask for the needle formation. Mo was sometimes self-supplied by the sputtering of the Mo substrate holder during the etching, but the uniformity of the needles could be best controlled by coating small amount of Mo before etching. If the amount of Mo or the pressure was not adequate, the needles did not form or formed only along the edge of the diamond grains. With the optimum condition, we could fabricate sharp diamond needles whose pillar diameter and height were 0.1 µm and 3 µm, respectively. The density was 30 needles/µm@super 2@. Since the needles were highly aligned and always formed in parallel with the field, the direction of the needles could be chosen by tilting the substrate. Not only the polycrystalline diamond films but also the high pressure/high temperature diamond and the natural diamond could be etched to form needles. Our diamond needles can be utilized as the field emission cathode tips, diamond fiber for composite materials, highly efficient heat sinks for their large surface area, and sensors.

11:20am **FP+VT-MoM10 Hermetic Sealing and Evacuation of Candescent's ThinCRT@superTM@***, **T.S. Fahlen**,* Candescent Technologies Corporation **INVITED**

Candescent has developed a full color, full video, power efficient display, the ThinCRT@superTM@ based on Spindt-type field emitters with very low voltage switching (<10.5 volt), and "high voltage" (6 KV) aluminized phosphors. Because of the high voltage used, the faceplate (anode/phosphor screen) and backplate (cathode) of the display are separated by 1.25 mm. This talk describes two methods used to hermetically seal the perimeter and evacuate ThinCRT displays. In both methods, the faceplate and backplate are sealed to a frame made of glass frit placed between them following an accurate, room temperature and atmospheric pressure alignment procedure. One sealing method uses a laser to first seal the frit frame to the faceplate, and then to hermetically seal the backplate to this assembly in a vacuum environment; no exhaust tubulation is required, and a non-evaporable getter is incorporated along one internal border of the display. A second method uses a laser to seal the frit frame to the faceplate, and the backplate to the frame/faceplate assembly but in a non-vacuum environment. An auxiliary chamber (AC) containing a getter and exhaust tube is then oven sealed to the rear of the assembly. Holes in the backplate allow the gases in the interior of the display to flow into the AC. The display assembly is then evacuated through an exhaust tubulation. The AC saves border space by allowing the getter to be removed from the display border to the rear of the display. The AC adds no additional thickness to the display because it protrudes no further than do the display electronics which are also attached to the rear of the display. In both sealing methods, the exact spacing between the faceplate and the backplate is determined solely by the internal support structure. The frit frame and sealing process have been designed so that during laser sealing, the frit expands to fill and seal the small gap left between the frit frame and the faceplate.

Magnetic Interfaces and Nanostructures Technical Group
Room 618/619 - Session MI-MoM

New Magnetic Materials

Moderator: B.T. Jonker, Naval Research Laboratory

8:20am **MI-MoM1 Role of Intergrowths in the Naturally Layered Manganites***, **S.D. Bader**,* Argonne National Laboratory **INVITED**

Doped LaMnO@sub 3@ yields the colossal magnetoresistance (CMR) family of perovskite materials. The physics is governed by competing interactions that include double exchange, super-exchange, Jahn-Teller effects, polarons, charge and spin ordering. To gain further insights, we have been exploring the properties of the related two-dimensional (2D) analogues that form a Ruddlesden-Popper series denoted SrO(LaMnO@sub 3@)@sub n@ where SrO barrier layers separate n-layers of Mn-containing oxygen octahedra. As in the perovskites, the La@super +3@ doped with Sr@super +2@ to yield the requisite mixed valent Mn@super +3@ and Mn@super +4@ needed for the CMR. We focus on n=2 (bilayers) and x=0.4 and 0.3, denoted SrO[(La@sub 1-x@Sr@sub x@)MnO@sub 3@)@sub 2@, which can be viewed as naturally occurring superlattices. They have reduced Curie temperatures relative to the 3D perovskites. Bulk single crystals grown in an optical image furnace are used. These structures are instructive because the competing interactions are now anisotropic. We illustrate examples of fascinating intrinsic and extrinsic behavior, including the intrinsic CMR values and the role of the extrinsic intergrowths on the magnetic properties. Intergrowths are stacking faults, such as occasional missing and/or extra octahedral layers. We find that intergrowths with extra octahedral layers can simulate 2D magnetic inclusions. Their magnetic and scaling properties provide a link to the 2D magnetism of artificially layered ultrathin ferromagnetic films. This work is supported by U.S. DOE BES-MS under contract #W-31-109-ENG-38.

9:00am **MI-MoM3 XPS Study of CMR Perovskite Thin Films: La@sub 0.65@D@sub 0.35@MnO@sub 3@ (D=Ca,Sr,Pb)***, P.A. Dowben,* University of Nebraska, Lincoln*; **H. Dulli**,* University of Tennessee, Knoxville*; B. Xu, Q.L. Xu, S.H. Liou,* University of Nebraska, Lincoln

Surface segregation phenomenon has been investigated in crystalline films of La@sub 0.65@D@sub 0.35@MnO@sub 3@ (D=Ca,Sr,Pb) by angular resolved XPS. We found that surface concentration of the dopant atoms is different from the bulk. Using a binary alloy model, we constructed depth profiles for the above dopants. The surface segregation was most significant in the case of Sr-doped films which also exhibit a surface insulating phase at low temperature as can be seen clearly from the binding energy shift in the core level spectra.

9:20am **MI-MoM4 Orientational Dependence of CMR Manganite Thin Films Observed with Ferromagnetic Resonance Spectroscopy***, **E.S. Gillman**,* Norfolk State University and Thomas Jefferson National Accelerator Facility*; N. Noginov,* Norfolk State University

Previously we have observed that transport properties depend on crystal orientation and morphology in CMR manganite thin films.@footnote 1@ Here we present ferromagnetic resonance (FMR) data that shows that these films exhibit different properties that depend on thier relative orientation in an applied magnetic field. Single crystal films exhibit larger saturization magnetization when the applied field is perpendicular to the surface, but in polycrystalline films the opposite is true. On all films there is a broadening of the resonance peak near the ferromagnetic-paramagnetic transistion temperature that is characteristic of critical fluctuations. @FootnoteText@ @footnote 1@"Crystallinity and Magnetoresistance in La@sub x@Ca@sub 1-x@MnO@sub 3@ Thin Films'', E. S. Gillman, M. Li and K. -H. Dahmen, J. Appl. Phys., 84, 6217 (1998).

9:40am **MI-MoM5 Ferromagnetic Semiconductor Heterostructures Based on (GaMn)As*, M. Tanaka,*** University of Tokyo, Japan **INVITED**

We have studied magnetic semiconductor (Ga@sub 1-x@Mn@sub x@)As thin films and III-V based magnetic heterostructures, and present their molecular beam epitaxial growth, structure, magnetic, transport, and magnetooptic properties. The present work, we believe, will give new opportunities to explore an interdisciplinary field between semiconductors and magnetics. (Ga@sub 1-x@Mn@sub x@)As thin films were grown by low-temperature molecular-beam epitaxy (LT-MBE) at 200C - 300C on GaAs(001) substrates. Homogeneous ternary alloys with the Mn content x up to ~0.10 were obtained, and the lattice constants of the zinc-blende (GaMn)As are slightly larger (< 0.4 %) than that of GaAs.@footnote 1@ The (GaMn)As thin films showed a ferromagnetic order with the Curie temperature of 10 K - 100 K. Systematic study indicates that the ferromagnetism of GaMnAs is induced by carriers (holes). The concept of bandgap engineering is well established in nonmagnetic semiconductors. Here, we demonstrate the successful growth of III-V based superlattice (SL) structures consisting of ferromagnetic semiconductor (GaMn)As and nonmagnetic semiconductor AlAs.@footnote 2,3@ Both x-ray diffraction and transmission electron microscopy showed that the SLs are formed with excellent crystal quality and abrupt interfaces. Magnetooptic spectra of these SLs have revealed that, due to quantum confinement effect, the interband transition is systematically blue-shifted with decreasing the thickness of GaMnAs, and that some higher subbands are formed. Furthermore, we have fabricated GaMnAs/AlAs/GaMnAs ferromagnetic tunnel junctions, and have demonstrated large tunneling magnetoresistance (TMR). The feasibility of preparing such magnetic quantum heterostructures based on (GaMn)As, we believe, will open up unique possibility of coupling spinrelated phenomena with the well-established band engineering in III-V semiconductors. @FootnoteText@ @footnote 1@ T. Hayashi, M. Tanaka, T. Nishinaga, H. Shimada, H. Tsuchiya, Y. Ootuka, 8th Int. Conf. on Molecular Beam Epitaxy, Malibu, August 1996, J. Cryst. Growth 175/176, 1063 (1997). @footnote 2@ T. Hayashi, M. Tanaka, K. Seto, T. Nishinaga, H. Shimada, K. Ando, Appl. Phys. Lett. 71, 1825 (1997). @footnote 3@ M. Tanaka, J. Vac. Sci. & Technol. B16, 2267(1998).

10:20am **MI-MoM7 Epitaxial Ferromagnetic Ni@sub 2@MnGa Film Grown on GaAs (001) by Molecular Beam Epitaxy*, J.W. Dong,*** *L.C. Chen, D.M. Carr, C.J. Palmstrom,* University of Minnesota

In the bulk, stoichiometric Ni@sub 2@MnGa is ferromagnetic with a Curie temperature 376°K. Above 202°K, the stable austenitic phase has the cubic L2@sub 1@ Heusler structure with a lattice parameter 3% larger than GaAs. This structure can be considered as a NaCl crystal structure of Mn and Ga with Ni in the tetrahedral sites. It may also be considered as an 'ordered' CsCl structure with a simple cubic lattice of Ni with every other interstitial site filled with Mn and Ga, respectively. The similarity in crystal structures suggests that metallic compounds with either the NaCl or CsCl structures should act as excellent templates for Ni@sub 2@MnGa growth. The growth of Ni@sub 2@MnGa on GaAs with a 6 ML-thick Sc@sub 0.3@Er@sub 0.7@As (NaCl structure) lattice matched to GaAs interlayer resulted in single crystal growth. In-situ reflection high energy electron diffraction patterns were streaky, indicative of high crystalline quality. Ex-situ X-ray diffraction and plan-view TEM selected area electron diffraction patterns confirmed single crystal growth and showed that a 300Å thick Ni@sub 2@MnGa grew pseudomorphically on GaAs. Considering the lattice mismatch, this seems surprising. However, we speculate that the epitaxy is stabilizing a new tetragonal phase of Ni@sub 2@MnGa with a = b = 5.65 Å, c = 6.12 Å and will present a model to explain this. Magnetic measurements using vibrating sample and superconducting quantum interference device magnetometers revealed the Ni@sub 2@MnGa to have in-plane magnetization and a Curie temperature ~320°K. The growth and properties of Ni@sub 2@MnGa films grown with a NiGa (CsCl structure) interlayer and directly on GaAs will be compared with ones grown on Sc@sub 0.3@Er@sub 0.7@As interlayers. The effect of the interlayer on the interfacial properties will also be discussed.

10:40am **MI-MoM8 MBE Growth and Characterization of bcc Fe@sub X@Co@sub 1-X@/GaAs(001) Heterostructures*, L.C. Chen,*** *B.D. Schultz, J.Q. Xie, C.J. Palmstrom,* University of Minnesota

We have successfully grown bcc Fe@sub X@Co@sub 1-X@ on GaAs(001) at 175°C by Molecular Beam Epitaxy. In-situ reflection high energy diffraction indicates a two dimensional growth mode of epitaxial bcc Fe@sub X@Co@sub 1-X@ on GaAs(001). A 40Å thick Al protective layer was deposited in-situ at a substrate temperature <0°C prior to removal from the MBE system. Ex-situ atom force microscopy studies show atomic steps indicative of a step-flow growth mode. X-ray diffraction data reveal an epitaxial orientation of bcc Fe@sub X@Co@sub 1-X@(001)||GaAs(001). A Rutherford backscattering spectrometry channeling minimum yield of @chi@=11% suggests good crystalline quality epitaxial bcc Fe@sub X@Co@sub 1-X@. Vibrating sample magnetometry measurements revealed in-plane magnetization and square hysteresis loops. In order to minimize interfacial reactions and diffusion during the Fe@sub X@Co@sub 1-X@ growth, we investigated the use of an epitaxial Sc@sub X@Er@sub 1-X@As diffusion barrier interlayer. Sc@sub X@Er@sub 1-X@As is thermodynamically stable on, and is lattice matched to, GaAs. Reflection high energy diffraction indicates a two-dimensional growth mode of epitaxial single crystal Fe@sub X@Co@sub 1-X@ film growth on the Sc@sub X@Er@sub 1-X@As surface at both 175°C and 470°C. Both ex-situ Rutherford backscattering spectrometry and in-situ Auger electron spectroscopy did not detect arsenic in Fe@sub X@Co@sub 1-X@ films. The effect of Sc@sub X@Er@sub 1-X@As thickness and Fe@sub X@Co@sub 1-X@ growth temperature on the growth mode and magnetic properties will be discussed. Further studies of interfacial transportation properties will also be reported.

11:00am **MI-MoM9 Low-temperature Gaseous Nitriding and Subsequent Oxidation of Epitaxial Ni/Fe Bilayers*, A.V. Mijiritskii,*** *M.A. James, D.O. Boerma,* University of Groningen, The Netherlands

Fe-nitrides are of interest due to their anti-corrosive, mechanical and magnetic properties. From a technological point of view, one of the most attractive ways to form Fe-nitrides is gaseous nitriding of Fe in a NH@sub 3@+H@sub 2@ mixture. The disadvantage of this method is the necessity to apply relatively high temperatures upon the nitriding. Lately, a method has been discovered allowing fabrication of pore-free Fe-N phases in a mixture of NH@sub 3@+H@sub 2@ at relatively low temperatures (550-625 K) by using a Ni cap-layer as a catalyst. In the present work we study the behaviour of epitaxial Ni/Fe bilayers upon low-temperature gaseous nitriding as well as the subsequent oxidation of the Ni/Fe-N systems formed. A number of experimental techniques was employed including XRD, RBS, XPS, and CEMS. Epitaxial Ni/Fe bilayers were grown on MgO(100) in-situ by molecular beam epitaxy (MBE) or ex-situ by laser ablation deposition (LAD). Nitriding was done in a dedicated N-oven at 575 K at different nitriding potentials of the NH@sub 3@+H@sub 2@ mixture depending on the nitride phase to be produced. Oxidation of the Ni/Fe-N systems obtained was performed in an O-oven at 525 K in P(O@sub 2@)=1x10@sup -6@ mbar. Upon nitriding in NH@sub 3@+H@sub 2@, oxidation of Fe was observed due to small fraction of H@sub 2@O present in the N-oven. On the basis of the RBS measurements it was concluded that to prevent the oxidation, the thickness of the capping Ni layer should exceed 200 Å. XRD measurements performed on as-nitrided samples revealed that Fe-nitride phases form at higher nitriding potential values in the case of epitaxial Ni/Fe bilayers compared to policrystalline Ni/Fe bilayers. This is probably due to the absence of nucleation sites in the epitaxial layers. The epitaxial relationships of the phases produced and the details of the nitriding and oxidation kinetics are being discussed.

11:20am **MI-MoM10 Epitaxial Growth of La-Ca-Mn-O Thin Film on Out-of-Plane Twinned LaAlO@sub 3@*, J.-H. Song,*** Korea Institute of Science and Technology, Korea*; K.K. Kim,* Korea Institute of Science and Technology, Seoul*; J.H. Song,* Korea Institute of Science and Technology*; D.-K. Choi,* Hanyang University, Korea*; Y.J. Oh, H.-J. Jung, W.K. Choi,* Korea Institute of Science and Technology, Seoul

LCMO thin film with 145 nm thickness was epitaxially grown on LaAlO@sub 3@ (100) substrate using RF magnetron sputtering. The crystalline structure of LCMO thin film on LaAlO@sub 3@ was characterized using backscattering (BS)/channeling and 4-circle X-ray diffractometer. Thin film grown at 600@sup o@C and 100 W shows the minimum channeling yield of 4.98%. XRD @theta@-rocking also showed the FWHM of 0.311@sup o@ for LCMO (200) peak, which is quite small compared to the previous reported values of 0.4@sup o@-0.5@sup o@. But the @theta@-rocking curve seemed to be composed of 2 peaks which was known due to strained-layer and relaxed-layer. In the RBS and BS/channeling study, only direction showed difference by 1.12@sup o@. In addition, we observed the substrate has the out-of-plane twinned structure from hight resolution XRD @theta@-rokcing on LaAlO@sub 3@ (200) peak. From above results, we confirmed the film with only strained layer was epitaxially grown on the out-of-plane twinned substrate. The full width at half maximum value of XRD @theta@-rocking on LCMO film (200) peak was 0.147@sup o@ after BS/channeling analysis. This value is smaller value than any other reported values of LCMO on LaAlO@sub 3@.

Manufacturing Science and Technology Group
Room 611 - Session MS-MoM
Advanced Design Methodologies and Factory Modeling

Moderator: S. Rauf, Motorola Inc.

8:40am **MS-MoM2 Aspect Ratio Dependent Etching**, ***T.S. Cale***, *M. Bloomfield, S. Soukane,* Rensselaer Polytechnic Institute

This presentation reviews a study of 'aspect ratio dependent etching' (ARDE); i.e., the effect of aspect ratio on etch rate in reactive ion etching (RIE) systems. The goal is to provide guidelines for etch process developers, and involve simple but flexible models for the transport and kinetics. EVOLVE, a deposition, etch and thin film flow simulator, is used to characterize the ARDE via an RIE 'lag parameter'. Further simulation is then used relate ARDE to the neutral-to-ion flux flux ratio, in the simplified transport and kinetic models. This flux ration ratio can be related to RIE operating conditions.

9:00am **MS-MoM3 SEMATECH's Plasma Modeling Project**, ***G.L. Bell***, *P.M. Ryan,* Oak Ridge National Laboratory **INVITED**

As wafer costs increase with size, the expenses associated with developing new tools and running process development experiments increase prohibitively. Robust plasma models and high-performance simulation tools are needed to reduce the significant cost of introducing new processing technologies. The goal of the SEMATECH Plasma Model Development project is to accelerate technology development through the advancement of predictive models for plasma etching. Three major barriers must be overcome to accomplish this goal: 1) the lack of detailed verified data on actual production tools to be used for testing the models and to support process development, 2) the need for gas phase and surface mechanisms for commercially relevant oxide and metal etch plasmas, and 3) the absence of a comprehensive database of detailed cross-sections of plasma etching gases for use by the modeling community. To address these hurdles, this SEMATECH project combines the efforts of universities and national labs into an integrated modeling effort. Supported research includes development of a relevant gas phase chemistry database through cross-section and reaction rate measurements and computations, development of surface reaction mechanisms from particle beam and in situ surface measurements during plasma processing, and experimental measurement of plasma parameters and ion/neutral species distributions on representative plasma reactors. The team produces "best known" database sets (gas phase, surface reactions, plasma diagnostics data and model inputs) to develop physical models for input into advanced codes which predict etch rate (selectivity) and uniformity. This presentation outlines the project structure, the role of the working groups and some representative data obtained to date. @FootnoteText@ G.L. Bell is currently on assignment to SEMATECH's Interconnect Division.

9:40am **MS-MoM5 A Comparison of Spectroscopic Measurements of an Inductive Plasma Source with the INDUCT Model**, ***M.L. Huebschman***, *J.G. Ekerdt,* University of Texas, Austin; *P.A. Vitello,* Lawrence Livermore National Laboratory; *J.C. Wiley,* University of Texas, Austin

Noninvasive spectroscopic measurements of an inductively driven hydrogen plasma source with density and temperature characteristic of plasma processing tools have been done with an ultimate application of cleaning of silicon substrates These measurements allow full radial and axial profiles of electron density and temperature to be measured from absolutely calibrated multichannel spectroscopic measurements of upper state number densities and a collisional radiative model. Profiles were obtained over a range of powers from 50 to 200 W and pressures from 5 to 50 mtorr in hydrogen in a small cylindrical source. The hydrogen working gas and simple cylindrical geometry was chose to simplify detailed comparisons with a 2D computational model (INDUCT95) which uses a fluid approximation for the plasma and neutral gas. The code calculates the inductive coupling of the 13.56 MHz RF source, the collisional, radiative, and wall losses as well as a complete chemistry model for H@sub 2@, H, H@super +@, H@sub 2@@super +@ and H@sub 3@@super +@. We found good agreement between the model and experimental data over part of the operational range. Ranges of agreement and divergence will be discussed.

10:00am **MS-MoM6 Characterization of Showerhead Performance at Low Pressure**, ***D.B. Hash***, ELORET; *T. Mihopoulos,* Motorola Inc.; *M. Meyyappan,* NASA Ames Research Center; *D.G. Coronell,* Motorola Inc.

The overall objective of this work is to characterize the flow through showerheads by deriving pressure drop versus velocity correlations that can be then used in reactor scale simulations where the showerhead is approximated as a porous medium. At relatively low Reynolds numbers (< 1-10 based on the hole length scale) and in the absence of slip flow, Darcy's Law, gradient P = µ U/ k, can be used to express the relation between the pressure drop and velocity where µ is the fluid viscosity and k is the permeability that can be theoretically predicted as k = e R@super 2@ /8, where e is the porosity. However, at sufficiently small hole diameters and decreased pressures (< 5 Torr), the Knudsen number based on showerhead tube radius increases, and the flow may be in a transition regime. Different expressions have been proposed to account for this effect in the permeability by expressing k as a function of either pressure or Knudsen number. But at even higher Knudsen numbers, the pressure drop - velocity dependence is non-linear, and Darcy's Law no longer holds such that a permeability cannot be defined. The direct simulation Monte Carlo method is used along side conventional CFD techniques to determine the extent to which the CFD technique is appropriate and helps to derive correlations for the more rarefied cases of interest in these showerhead flows.

10:20am **MS-MoM7 IMP-PVD Equipment Level Process Analysis Using Simulation**, ***P.L.G. Ventzek***, *S. Rauf, D.G. Coronell, V. Arunachalam, X.-Y. Liu, J. Arnold, D. Denning, S. Garcia, A. Korkin,* Motorola Inc.; *Y.-K. Kim,* National Institute of Standards and Technology

Ionized metal plasma physical vapor deposition continues to be viewed as a promising means of depositing seed and barrier layers in tight critical dimension high aspect ratio features. Issues that require attention at the equipment level deal with obtaining sufficient film continuity and conformality in a uniform way across a wafer. Critical to these metrics are the delivery of the appropriate net ion current (both metal and inert) and ionization fraction of the metal flux (energy distribution and angular spread). Also important may be the energy content brought to the surface by excited state species. We have characterized these parameters using HPEM (University of Illinois) and will present a comparison between the model predictions for DOE's performed on a Cu IMP-PVD chamber. Of note from this study is the sensitivity of predicted behavior on the capacitive-inductive power distribution from the inductive coils. Very high percentages of the power delivered to the coil are lost capacitively and the fraction in very sensitive to the power capacitively coupled to the wafer. The role of metastable species generated in the plasma is also investigated. Metastable species are usually thought only to play the role of facilitating relatively low energy pathways for ionization . It turns out that heavier metals have a wealth of metastable states even at very low energy allowing them to alter the plasma behavior and to facilitate different processes at the surface when compared to lighter atomic number metals.

10:40am **MS-MoM8 Holistic Yield Learning Methodology**, ***A.J. Strojwas***, PDF Solutions Inc. **INVITED**

Each year, IC manufacturers invest billions of dollars in new equipment in an attempt to increase their competitiveness by delivering enhanced performance and more functionality at a lower cost. Success in today’s marketplace requires successful technology integration under increasing market pressure to deliver products as quickly as possible. Unfortunately, standard yield improvement practices focus too narrowly on defect elimination and use techniques that solve yesterday’s not today’s problems a comprehensive view of yield learning. To ensure profitability, a new approach to yield learning must be developed. Inevitably, these changes require a re-defining of the interfaces between design, test and manufacturing. In this paper, we present a comprehensive view of the yield problem and a "holistic" yield ramping methodology specifically designed to significantly reduce the yield ramp time by eliminating not only defects, but also by resolving parametric and systematic problems. Manufacturing defect data, process recipe, and design information are analyzed simultaneously, to derive a much deeper understanding and subsequent solution to the process and design architecture issues that affect yield and performance. In combination with the use of simulation and a hypothesis-driven work style, this approach delivers increased yield and performance in a fraction of the time required by traditional methods.

11:20am **MS-MoM10 Particle Simulations of Chemically Reacting Plasmas*,* *M.A. Gallis*,** *T.J. Bartel,* Sandia National Laboratories

This work focuses on the development of a particle simulation code that can be used for the modeling of low pressure inductively coupled high density plasma reactors. The code is based on the Direct Simulation Monte Carlo methodology where a relatively small number of particle simulators mimic the behavior of a large number of real particles. Only heavy particles (ions and molecules) are directly modelled. The electron number density is deduced from this of the ions assuming local charge neutrality. Since the plasma sheathes are very small the assumption of charge neutrality is used through out the computational domain. The electron temperature is calculated using two different methods. The first one uses an electron energy equation using ICP power electron conduction and inelastic electron impact reactions. The second one uses a kinetic treatment of the electrons creating an equilibrium distribution of electrons every time an estimation of the electron temperature is needed. The motion of the electron gas is then followed in a fully kinetic fashion and for a time period short enough to assume that the heavy particles remain in their positions. The ICP power deposition for both methods is determined by an external code from Oakridge National Laboratories, ORMAX. The neutral-neutral and neutral ion interactions are directly modeled. The two methods will be compared for two electro-negative systems; pure CL2 and C2F6 in the GEC test cell geometry.

11:40am **MS-MoM11 Simulations of Low Field Helicon Discharges@footnote 1@*,* *R.L. Kinder*,** *M.J. Kushner,* University of Illinois, Urbana

Due to their high ionization efficiency, ability to deposit power within the volume of the plasma and ability to operate at low pressures, helicon reactors are attractive for downstream etching and deposition. The power coupling of the antenna radiation to the plasma is a concern due to issues related to process uniformity when using high magnetic fields (100s G to kG). Operating at low magnetic fields (< 100 G) is therefore preferred to provide more uniform ion fluxes and to reduce the cost of the tool. To investigate helicon operation over large ranges of magnetic fields a full tensor conductivity has been incorporated into the electromagnetics module of the Hybrid Plasma Equipment model (HPEM) augmented by an effective collison frequency to account for Landau damping. Plasma properties for helicon excitation of Ar, Ar/N@sub 2@ and process relevant gases (CF@sub 4@, C@sub 2@F@sub 6@) as a function of magnetic field strength, field configuration and power will be discussed. Results of an argon plasma excited by a m = 0 mode field operating at 13.65 MHz shows a resonant peak in the plasma density occuring in the low magnetic field range and is attributed to off-resonant cyclotron heating. The transition from inductive coupling to helicon mode appears to occur when the fraction of power deposited through radial and axial fields dominates. Results from HPEM-3D will be used to resolve helicon wave structure in the m = 1 and -1 modes. @FootnoteText@ @footnote 1@This work was supported by SRC, AFOSR/DARPA, Applied Materials and LAM Research.

Nanometer-scale Science and Technology Division
Room 6C - Session NS-MoM

Nanotechnology

Moderator: H.G. Craighead, Cornell University

9:00am **NS-MoM3 Nanotechnology - Fiction, Fad or Future?*,* *J.S. Murday*,** Naval Research Laboratory **INVITED**

Nearly 20 years have passed since Binnig and Rohrer published the first STM paper. This is the traditional gestation period for maturation of science into technology. What are the prospects for the science of nanostructures leading to new technology? There is already significant technology based on empirically derived nanostructures (for instance, heterogeneous catalysts, photographic film). A broad base of new nano-analytical tools is in place; nano-fabrication techniques are improving; new products are appearing in the market; and Federal funding agencies are taking notice. The National Science and Technology Council has formed an Interagency Working Group on Nanometer Science, Engineering and Technology. The working group will issue a report (June 1999) summarizing the opportunities, suggesting a national initiative in nanotechnology, and recommending a substantially larger federal investment in the science necessary to accelerate technologies built on nanostructures. This talk will briefly review the SOA in nanoscience, focus on highlighting examples where AVS pertinent nanoscience is making the transition into technology (computer memory-terabit/in2, biological sensors-molecular recognition/signal transduction, and nanostructured coatings-surface engineering), and conclude with a glimpse at potential federal agency funding.

9:40am **NS-MoM5 A Report on the Workshop "Vision for Nanotechnology R&D in the Next Decade"*,* *R.S. Williams*,** Hewlett-Packard Labs **INVITED**

More than 70 scientists, engineers, program directors and senior administrators from a broad array of disciplines, institutions and geographical regions gathered from January 27-29 in Washington, DC to discuss their views on the future of Nanotechnology research. This workshop was sponsored by the Interagency Working Group on Nano Science, Engineering and Technology (IWGN), which in turn has been charged by the Committee on Technology of the Office of Science and Technology Policy to identify the trends in nanotechnology, establish federal R&D priorities, and provide budget guidance to ensure that the potential of nanotechnology can be achieved in the US. Representatives from academic, corporate and government research organizations with backgrounds in dispersions and coatings, electronics broadly defined, composite structural materials, biology, medicine, energy and environmental sciences discussed technical issues and appropriate funding strategies. Given the large and heterogeneous nature of the workshop attendees, there were a surprising number of scientific themes that emerged as being crucial across the spectrum of research areas, such as ripening. If there were consensus issues among the attendees, they were most probably "Nanotechnology does not yet exist, but it will develop rapidly over the next decade", "avoid hype and extravagant promises", "the best federal investment strategy is to back a broad spectrum of high quality basic research and not focus on specific applications too soon", "focus the majority of funding on individual researchers and small interdisciplinary teams", and "the creation of nanotechnology will require the collaborative efforts of transdisciplinary teams and will in turn transform many traditional disciplines". This presentation will describe some of the accomplishments of current nanoscience research, opportunities for the future that were identified, and recommendations for funding agencies that came out of the workshop.

10:20am **NS-MoM7 Experimental and Theoretical Coincidence in Room Temperature Single Electron Transistor Formed by AFM Nano-Oxidation Process*,* *Y. Gotoh*,** *K. Matsumoto, T. Maeda,* Electrotechnical Laboratory MITI, Japan*; S. Manalis,* Massachusetts Institute of Technology*; J. Harris, C. Quate,* Stanford University

The experimental results of the room temperature operated single electron transistor (SET) were simulated using orthodox theory and 3 dimensional Poisson's equation. The simulated results coincided well with the experimental results. The planer type SET has been fabricated by oxidizing the surface of 2nm-thick titanium (Ti) metal that was on the atomically flat @ALFA@-Al@sub 2@O@sub 3@ substrate using the pulse mode AFM nano-oxidation process@super 1)@. The narrow oxidized Ti wire works as a tunnel junction for SET. The fabricated SET shows Coulmb oscillation characteristic even at room temperature at the drain bias of V@sub D@=0.3V when the gate bias was changed from V@sub G@=0 to 10V, and 5 oscillation peaks were observed with the periods of ~2V. The drain current was modulated by the gate bias and oscillates from 2.4pA to 3pA. Therefore, the modulation rate is ~20%. Using the orthodox theory, the experimental Coulmb oscillation was fitted using the parameters of the gate capacitance CG=8x10@super-20@F and the tunnel junction capacitances C@sub 1@=C@sub 2@=2.9x10@super -19@F. The simulated result represents well the experimental one, i.e. the position and the number of the Coulmb oscillation peaks and the modulation rate of the drain current coincide with the experiment of ones. Furthermore, tunnel junction capacitances were calculated by solving the 3D Poisson's equation for the structures of fabricated SET. In the calculation, the error tolerance of 0.01% was used. The calculated tunnel junction capacitances is found to be C@sub 1@=C@sub 2@=4x10@super-19@F which is almost coincide with the parameter used in the orthodox simulation. For further improvement of SET characteristics, an ultra sharp multi-wall carbon nanotube AFM tip was introduced for the AFM nano-oxidation process to reduce the oxide wire width down to 10~15nm to increase a tunnel current to improve S/N ratio of SET. 1) K. Matsumoto, Proceedings of IEEE Vol. 85, No. 4, p. 612 (1997).

10:40am **NS-MoM8 Study of the Super-resolution Near-field Structure for Optical Storage*,* *F.H. Ho*,** *D.P. Tsai, C.W. Yang,* National Chung Cheng University, Taiwan

We present the study of the mechanism of surface plasmons enhanced super resolution near-field structure, glass/SiN/Sb/SiN, for optical storage.

Nonlinear near-field optical effects of the glass/SiN/Sb/SiN on the transmitted light spot were experimentally observed by a tapping-mode tuning fork near-field scanning optical microscope. Imaging results of the near-field intensity gradients showed that focused light spot through the super resolution optical near-field structure, glass/SiN/Sb/SiN, consists of a normal propagating term and an evanescent term resulting from the laser-excited surface plasmon of the Sb thin film. Results also demonstrated the spot size of the evanescent field intensity can be manipulated by the detecting sensitivity of PMT, while the spot sizes of the propagating intensity remained the same. The working principle of the reduction of the focused spot size and the transfer of near-field photo-thermal energy from Sb/SiN interface to the recording layer are explained.

11:00am **NS-MoM9 Nanometer-scale Science of Conjugated Polymer Interfaces**, ***A.R. Burns***, *R.W. Carpick, D.Y. Sasaki,* Sandia National Laboratories

Highly-ordered organic films with integrated conjugated backbones and functionalized tail groups have considerable promise in several areas of nanometer-scale science and technology, especially sensor development. This technology brings together synthetic strategies, self-assembly and Langmuir-Blodgett deposition, and scanning probe characterization of both structural and optical responsivities. Specifically, we will discuss recent developments in the preparation and analysis of polydiacetylene monolayers on silica and mica substrates. As confirmed by atomic force microscopy and fluorescence microscopy, the monolayers consist of domains of linearly oriented conjugated backbones with pendant hydrocarbon side chains above and below the backbones. The backbones impose anisotropic packing of the hydrocarbon side chains which leads to a 300% friction force anisotropy. Phase transitions of the polymer induced by localized mechanical strain or chemical binding will also be discussed in terms of optical and morphological changes. Finally, we will discuss results concerning the incorporation of these polymers into three-dimensional nanocomposites. 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.

11:20am **NS-MoM10 Fabrication of Nanostructures by Laser Focusing of Fe Atoms**, ***R.C.M. Bosch***, *K. van Leeuwen, H.C.W. Beijerinck,* Eindhoven University of Technology, The Netherlands

We present an improved atom lithography method for the production of nanomagnetic wires and dots having well defined shape and separation. It is based on laser manipulated deposition of a supersonic beam of Fe atoms. The nodes of a 372 nm standing light wave act as a perfect lens for an incoming monochromatic parallel atomic Fe beam. The feature size of the deposited structures is therefore first of all limited by the quality of the incoming beam, and secondly by spherical aberration. A parallel beam is obtained by well known laser cooling techniques, but our improvement lies in the reduction of chromatic aberration by using a self-developed Fe evaporation source seeded with high pressure argon gas. The mixture will expand supersonically and due to adiabatic cooling it is in principle possible to obtain a beam with an axial velocity spread of less than 10%. The problem of spherical aberration will be solved with beam masking: a transmission grating with 100 nm slit sizes upstream of the standing wave allows only atoms near the nodes to be deposited. With the presented method we expect to reduce the structure sizes produced by conventional atom lithography methods and to break the 10 nm limit.

11:40am **NS-MoM11 One-dimensional Nanostructure of SiCN Single Crystal**, ***P.F. Kuo,*** National Taiwan University, Taiwan*; C.-Y. Wen,* National Taiwan University*; F.G. Tarntair,* National Chio Tung University, Taiwan*; J.-J Wu,* Institute of Atomic and Molecular Sciences, Taiwan*; S.L. Wei,* Fu-Jen University, Taiwan*; K.H. Chen,* Academia Sinica, Taiwan*; L.C. Chen, Y.F. Chen,* National Taiwan University

Nanostructural materials have attracted wide attention due to its fundamental confinement effect and further applications of composites and microelectronics. From the standpoint of one-dimensional structures, there has been significant speculation about structures and properties of nanotubes and nanorods. In this paper, we report the growth of a novel one-dimensional single crystal nanorod comprised of Si, C, and N using microwave plasma enhanced chemical vapor deposition (MWCVD). The transmission electron microscopic analysis shows that the nanorods are of 1.5 µm in length and 50 nm in diameter, and the lattice images indicate that they are single crystals. High-resolution scanning electron microscope further confirms the nanorod diameter ranging from 10 to 60 nm, with hexagonal cross-section. The stoichiometry of the crystal was examined by the energy dispersive X-ray spectrometer (EDX) and the results showed a Si, C, N atomic ratio of 1:2:1. Detailed structural and stoichiometry information as well as optical and electronic properties measured by photoluminescence (PL) and electron field emission measurement are reported in this paper.

Organic Electronic Materials Topical Conference
Room 616/617 - Session OE+EM+FP-MoM

Organic Devices

Moderator: A. Kahn, Princeton University

8:20am **OE+EM+FP-MoM1 Invited Paper***,* ***C.W. Tang***, Eastman Kodak Company **INVITED**

NO ABSTRACT SUBMITTED.

9:00am **OE+EM+FP-MoM3 Ultrafast Electron Relaxation in Excited, DCM Doped Alq Films**, ***K. Read***, University of Michigan*; H.S. Karlsson,* Royal Institute of Technology, Sweden*; M.M. Murnane, H.C. Kapteyn,* University of Michigan*; R. Haight,* IBM T.J. Watson Research Center

Electrons photoexcited into the lowest unoccupied molecular orbital (LUMO) of Alq (tris(8-hydroxyquinoline)aluminum) films doped with DCM (4-dicyanomethylene-2-methyl-6-p-dimethylaminostyryl-4H-pyran) have been studied using excite-probe laser photoemission. DCM doping, achieved by co-evaporation with Alq, is an important means of color tuning and enhancing Alq organic LED emission. In addition, DCM doped Alq films have been shown to lase at low photoexcitation thresholds. A detailed understanding of the involved relaxation mechanisms is beneficial to both applications. Using 3.14 eV excite, and 26.7 eV probe, 100 femtosecond laser pulses, we have observed the LUMO decay rate over the first 175 picoseconds, during which time diffusion is insignificant, and all dynamics occur in the absence of electron transport. We have found that the LUMO population fits to a model wherein the majority of the excitation rapidly transfers from the Alq to the DCM and decays via stimulated emission in the DCM, concentration quenching in the DCM, and bimolecular singlet-singlet annihilation in both the Alq and the DCM. Increasing either the DCM doping percentage, or the excitation intensity, is seen to significantly enhance the early, fast processes. The occupied to unoccupied molecular orbital energy gap shrinks as a function of excite-to-probe delay, in accordance with the expected energy relaxation within the excited states. Pure DCM yields a correspondingly smaller energy gap, and rapid LUMO decay. Analyzing the LUMO decay mechanisms allows an improved understanding of the functions served by DCM doping of Alq films.

9:20am **OE+EM+FP-MoM4 Unoccupied Molecular Orbitals in Organic Electroluminescent Materials Studied by Femtosecond Harmonic Photoemission**, ***H.S. Karlsson,*** Royal Institute of Technology, Sweden*; K. Read,* University of Michigan*; R. Haight,* IBM T.J. Watson Research Center

We have studied the lowest unoccupied molecular orbital (LUMO) in three organic electroluminescent materials using pump-probe harmonic photoemission based on a femtosecond laser system. The energy gap between the LUMO and the highest occupied molecular orbital (HOMO) in thin films of the blue-light-emitting molecules bis(2-methyl-8-quinolinolato)(para-phenyl-phenolato)aluminum (BAlq) and 1,4-bis(2,2-diphenylvinyl)biphenyl (DPVBi) was established and compared with the green-light-emitting molecule tris(8-hydroxyquinoline)aluminum (Alq). We have also studied the LUMO decay characteristics for the three materials and relate the differences in decay times to the morphology of the evaporated thin films. The effect on the electronic structure of the organics induced by deposition of metallic overlayers will also be shown and discussed.

9:40am **OE+EM+FP-MoM5 Femtosecond Charge Transfer Processes in Organic Molecular Heterostructures**, ***A.J. Mäkinen***, *S. Schoemann, Y. Gao,* University of Rochester*; M.G. Mason, A.A. Muenter,* Eastman Kodak Company*; A.R. Melnyk,* Xerox Wilson Center for Research & Technology

The charge transfer (CT) process in organic semiconductor heterostructures is an important problem for applications such as photoreceptors and light-emitting devices. The operation of a photoreceptor structure is based on a CT process at the interface of a charge generator layer and a charge transport layer. We have investigated such a structure formed by vacuum grown thin films of two organic molecules, N,N'-diphenethyl-3,4,9,10-perylenetetracarboxylic-diimide (DPEP) and N,N'-diphenyl-N,N'-(3-methylphenyl)-1,1'-biphenyl-4,4'-diamine (TPD), with femtosecond time-resolved photoemission spectroscopy (TR-PES). By measuring the lifetimes of the excited electron states in the mixtures and in the bilayer structures of these molecules, and by recording the UPS spectra of the films we are able to determine the time-scale and the energy regime for the CT process. Our results show that the CT takes place in less than 10 fs between the DPEP and the TPD molecules. We also demonstrate the significance of the film interface in separating the charges upon CT.

10:00am **OE+EM+FP-MoM6 A Comparison of Organic Light-Emitting Devices Using Transient Current-Transient Voltage, Transient Brightness-Transient Voltage, and Transient Brightness-Transient Current Analysis***, **B.J. Norris**, J.F. Wager,* Oregon State University*; J. Liu, Y. Yang,* University of California, Los Angeles

Four types of organic light-emitting devices (OLEDs) are compared using transient current-transient voltage [i(t)-v(t)], transient brightness-transient voltage [b(t)-v(t)], and transient brightness-transient current [b(t)-i(t)] analysis.@footnote 1@@footnote 2@ These analysis methods consist of obtaining the instantaneous brightness [b(t)], current [i(t)], and voltage [v(t)] of the device under test when it is subjected to a bipolar, piecewise-linear applied voltage waveform and then plotting these quantities parametrically. The four types of OLEDs considered are: two types of green OLEDs and a blue OLED, provided by the Eastman-Kodak Co., and a polymer light-emitting device (PLED) fabricated at the UCLA. The OLEDs are dual-layer heterostructures, involving an electron transport layer (ETL) and a hole transport layer (HTL). In contrast, the PLED is a single-layer device. The ETL and HTL capacitances of heterostructure OLEDs can be estimated from b(t)-i(t) curves. The b(t)-v(t) curves allow the conduction current to be estimated. Perhaps the most interesting aspect of this study is the existence of a small bump in the retrace portion of i(t)-v(t) curves of heterostructure OLEDs, which is not observed in single-layer PLEDs. This bump is ascribed to the removal of accumulated holes at the ETL/HTL interface. Hole accumulation at the ETL/HTL interface of OLED heterostructures is manifest as hysteresis in b(t)-v(t) curves. @FootnoteText@ @footnote 1@B. J. Norris, J. P. Bender, and J. F. Wager, "Steady-State Transient Voltage-Transient Current Characterization of OLEDs," SID Digest, in press. @footnote 2@ B. J. Norris, "Characterization of Organic Light-Emitting Devices," MS Thesis, Oregon State University, 1999.

10:20am **OE+EM+FP-MoM7 Organic and Polymer Transistors: Device Physics, Functional Blocks, and Circuits***, **A. Dodabalapur**, B.K. Crone, Y.Y. Lin, J.A. Rogers, S. Martin, R. Sarpeshkar, Z. Bao, W. Li, H.E. Katz, V.R. Raju,* Bell Laboratories, Lucent Technologies **INVITED**

This presentation will begin with a description of the basic physics of typical organic and polymer transistors and the factors which determine and influence the apparent mobility. The transient characteristics organic transistors with sub-microsecond switching speeds will be described. The integration of organic light emitting diodes and transistors is promising for emissive displays. We have developed designs for ‘smart’ pixels in which an analog circuit consisting of 6-7 transistors drives each LED. The simulated and experimental characteristics of such pixels will be presented. The development of air-stable n-channel organic transistors led to our demonstrating the first organic complementary circuits. The design considerations and characteristics of organic complementary circuits with > 100 transistors will be described. The noise properties of organic transistors and their use in gas sensors will be described.

11:00am **OE+EM+FP-MoM9 Sub-microsecond Switching of n and p-Channel Organic Field Effect Transistors***, **B.K. Crone**, A. Dodabalapur, Z. Bao, W. Li,* Lucent Technologies, Bell Laboratories

Steady state and transient electrical characteristics are presented for p-channel (@alpha@,@omega@-dihexyl quinquethiophene) and n-channel (copper hexadecaflourophthalocyanine) organic field effect transistors. The structure of the transistor is as follows. The gate electrode is a doped silicon wafer with a thermal oxide gate oxide. Gold source and drain contacts are evaporated and photolithographically defined on the oxide, and finally the active organic film is evaporated. The transistors measured had channel length of 4 µm and width 250 µm. Field effect carrier mobilities are determined for both the steady state and transient response using a simple model for the saturated drain current. The steady state mobility and threshold voltage were determined by a linear fit to the square root of the saturated drain current versus gate voltage. Steady state mobilities of 1.5x10@super -2@cm@super 2@/Vs for the p-channel and 3x10@super -2@cm@super 2@/Vs for the n-channel were measured. Transient mobilities were determined using the same model for the saturated drain current and the threshold voltage obtained in the steady state case. Transient mobilities were higher, 3x10@super -2@cm@super 2@/Vs for the p-channel and 1.5x10@super -1@cm@super 2@/Vs for the n-channel devices. The transient responses showed switching times less than 1 µsec for both p and n-channel devices.

Plasma Science and Technology Division
Room 609 - Session PS-MoM

Plasma Damage

Moderator: C.T. Gabriel, VLSI Technology

8:20am **PS-MoM1 Mechanisms and Dependencies of Gate Oxide Degradation Due to Electron Shading***, G.S. Hwang, **K.P. Giapis**,* California Institute of Technology

We present results form self-consistent Monte Carlo simulations of charging during etching of dense antennas in uniform high-density plasmas. The simulations include sheath dynamics, ion and electron transport in the trench spaces, feature charging, electron tunneling through thin gate oxides and surface charge dissipation. Charging maps are used to illustrate how electron shading causes differential microstructure charging and subsequently electron tunneling from the substrate. The magnitude of this current is employed as a measure of the extent of damage to the gate oxide. The calculations explain experimental trends regarding electron and ion temperatures and suggest ways to reduce the damage by manipulating plasma parameters. A surprising sub-linear relationship between damage and antenna area is explained by a decrease in the net ion current density collected by the structure due to charging potential changes.

8:40am **PS-MoM2 Calculation and Measurement of Ion and Electron Shading Parameters and Comparison with Computer Simulation***, **S.C. Siu**, R. Patrick, V. Vahedi,* Lam Research Corporation

Electron shading is recognized as a major mechanism for plasma process induced damage in commercial plasma etch chambers. As the semiconductor industry moves to smaller feature sizes and thinner gate oxides, shading induced damage becomes a greater concern. The shading effect is known to be more severe with higher aspect ratio features and high density plasmas. Recently, V. Vahedi, et al, derived an analytic model@footnote 1@ capturing the main parameters involved in electron shading. Two of these parameters, the ion and electron shading coefficients k@sub i@ and k@sub e@, have not been measured to date, but are crucial to the model. This study uses patterned and unpatterned SPORT@footnote 2@ wafers to measure and derive these shading parameters. In addition, a PIC simulation was used to predict values for these shading parameters. The simulation is able to account for charged resist structures that cause electron shading. Comparisons were made between the simulation and the experimental results. @FootnoteText@ @footnote 1@V. Vahedi, et al, "Topographic Dependence of Plasma Charging Induced Device Damage." 2nd International Symposium on Plasma Process-Induced Damage, May 13-14, 1997, Monterey California. @footnote 2@S. Ma and J.P. McVittie, Proceedings of the Symposium on Process Control, Diagnostics and Modeling in Semiconductor Manufacturing I, 95-4, pg 401, (1995).

9:00am **PS-MoM3 Direct Experimental Determination and Modeling of VUV induced Dielectric Conduction during Plasma Processing***, **M.V. Joshi**, J.P. McVittie, K.C. Saraswat,* Stanford University

The processing plasma provides a source of high intensity VUV (vacuum ultra-violet) light which is incident on IC dielectrics. It also sets up considerable electric fields across these dielectrics due to either non-uniformity or electron shading induced plasma charging. This is expected to cause photo-current flow in these dielectrics. These photo-currents can damage the underlying devices through a variety of mechanisms and change the charging profiles due to electron shading during plasma processing. Thus determination of the relationships between incident photon density, photon wavelength, applied electric field and photo-current density is vital not only to understanding and controlling photo-current damage to devices during plasma processing but also to accurately model electron shading damage mechanisms. In this work we study the photo-currents that flow through the bulk of the dielectrics as opposed to those flowing on the surface. Bulk photo-conduction would explain the damage seen during dielectric depostion in a plasma chamber. We use a high density plasma as the source of VUV light and a independent very low density plasma separate by a thin filter/window to provide the electric fields and also to act as the current source for the VUV induced photo-currents. This allows independent variation of UV intensity and plasma charging electric fields. The probe consists of a bare polysilicon pad and a nearby similar pad covered with the dielectric. These pads are biased using a voltage source and current drawn through them is measured allowing the determination of the current density - electric field characteristic for the given dielectric independent of the biasing plasma. We measured photo-current density versus applied electric field, dielectric thicknesses, dielectric types, incident photon density, incident photon wavelength, transient effects and in dual dielectrics. We propose a model to explain these effects based on hole trapping and electric field dependent hole-electron recomibination cross-section in the dielectric. This model allows prediction of VUV photo-conduction damage in realistic semiconductor processing structures.

9:20am **PS-MoM4 Investigating Ion Density and Electron Temperature Effects on Plasma Damage during Pulsed and Continuous Wave Metal Etching***, **K.H.A. Bogart**,* Lucent Technologies*; J.I. Colonell,* Praelux*; M.V. Malyshev, V.M. Donnelly, J.T.C. Lee,* Lucent Technologies

Plasma induced damage across gate oxides has been shown to decrease with the use of pulsed rf source power, although the basis for the reduction in damage is not yet well understood. During the pulsed plasma off time, positive ion density (n@sub i@@super +@), electron temperature (T@sub e@), and electron density generally decrease, reducing the current flux to the wafer and the potential difference across the substrate sheath. Near the end of the off time, negative ions are thought to cross the diminished sheath and neutralize charge on the wafer surface, and also to be the predominant negative charge carrier in the plasma. Langmuir probe measurements of n@sub i@@super +@ and T@sub e@ were made on a LAM 9600-PTX commercial metal etcher using blanket SiO@sub 2@, Al, and TiN films as well as during etching SiO@sub 2@-masked TiN/Al/Ti/TiN while reactor pressure (5-30 mTorr), rf source power (0-400 W), rf substrate bias power (0-200 W), pulse duty cycle (0.5 - 1), and pulse period (0.100 - 1000 ms) were varied. Plasma induced damage was quantified on wafers with 0.25 µm linewidth technology NMOS and PMOS damage testers etched under the conditions listed above. For a 50% duty cycle, 100 µs pulse period, typical I-V curves (asymmetric about zero current) were collected with substrate bias applied. Without substrate bias, I-V curves characteristic of an ion-ion plasma (symmetric about zero current) were observed from 0-15 µs and from 80-100 µs. I-V curves acquired with only substrate bias power (continuous RIE mode) were similar in shape to I-V curves taken at the end of the pulse off time with bias applied. T@sub e@'s decrease and then increase near the end of the off time, indicating that the substrate rf bias power is sufficient to sustain a plasma during the off time, and that negative ions are not able to cross the sheath. Implications for plasma damage mechanisms will also be discussed.

9:40am **PS-MoM5 Sources of Plasma Induced Damage in Back-End VLSI Processing***, **S.W. Downey**, D.W. Hwang, N. Layadi, P.W. Mason, A. Yen, V.M. Donnelly, M.V. Malyshev,* Lucent Technologies, Bell Laboratories*; J.I. Colonell,* Praelux, Inc. **INVITED**

The possibility of plasma induced damage of devices during wafer processing exists in both etch and deposition steps using gaseous discharges. A variety of mechanisms exist for deleterious current flow through a thin (25 @Ao@) transistor gate oxide. Plasma induced damage, as measured by gate leakage currents or shifts in threshold voltages, are given for several etch and deposition processes. Device damage during metal etch is shown to be related to aspect ratio and measured electron temperature. Evidence of current or voltage-limited conditions can be extracted by modeling. Cleaning and photoresist stripping plasmas can also cause damage if not properly designed or operated. Charging of photoresist while stripping is shown to be avoidable. Damage from plasma based metal deposition tools and via etchers is also problematic and difficult to decouple. Data will show that damage is sensitive to both hardware and process parameters, but improved hardware can yield a larger damage free process window.

10:20am **PS-MoM7 Charge Density Measurements in a Metal Etch Strip/Passivation Chamber***, **R.L. Jarecki**, M.G. Blain,* Sandia National Laboratories*; J.S. Papanu,* Applied Materials, Inc.

Manufacturers have increasingly incorporated chambers capable of resist stripping as well as in situ passivation of etch residues on their metal etch tool platforms to mitigate corrosion resulting from exposure to atmospheric moisture. Such chambers typically feature a downstream microwave collisional plasma source with a pressure in the 0.5 to 10 Torr range using multiple-step chemistries based mainly on O@sub 2@ (for fast resist strip) and H@sub 2@O (for passivation by chlorine scavenging). Although "downstream" plasma strip processes are usually presumed to be almost charge-free due to the rapid decay of plasma density away from the source, it may be advantageous in practice to allow some level of charge to survive in order to increase the flux of etchant species to the wafer, and hence throughput. This study reports the direct measurement of ion current densities observed via Langmuir probe in a commercial in situ strip and passivation chamber, for various gas feeds and hardware configurations, to help assess the level of charging damage to actual devices. Wafer level ion current densities below 2x10@super -8@ A/cm@super 2@ for typical strip processes and 8x10@super -10@ A/cm@super 2@ for passivation processes were observed with a standard gas distribution baffle configuration, while modified baffle configurations resulted in somewhat higher ion currents. Increases in power or total flow rate tended to increase current density. Correlation of probe measurements to surface photovoltage and antenna structure data will also be discussed@footnote 1@. @FootnoteText@ @footnote 1@Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract No. DE-AC04-94AL85000.

10:40am **PS-MoM8 Evaluation of Tests to Examine Charging Damage in Ion Implantation and Plasma Processes***, **M.J. Goeckner**,* Varian Semiconductor Equipment Associates*; J. Erhardt,* AMD Inc.*; S.B. Felch,* Varian Semiconductor Equipment Associates*; K. Ahmed,* AMD Inc.

Charging damage is a critical issue in both plasma processing and ion implantation systems. Charging damage is typically studied with one of several distinct types of test structures. One of the more common is an "antenna" MOS capacitor test structure. After the device is subjected to the charging environment, plasma or implantation, the gate dielectric is then analyzed for damage. For this paper, we will examine three analysis techniques on various dielectrics. These analysis techniques are: measurement of temporal change in induced voltage at a low current density (dV/dt); measurement of induced leakage current at a low voltage (~2 V); and measurement of induced voltage at a high, stressing, current density (~1 A/cm@super 2@). Damage to the dielectric will be induced with a controlled damage current, of known length and strength. Dielectrics will range from 100 Å oxide to sub-40 Å nitrided oxides. The purpose of this work is to determine the most appropriate technique for characterizing plasma charging dielectric degradation in the ultra-thin dielectric regime, as well as to gain a baseline understanding of the damage under controlled conditions. It is envisioned that the results of this study can be used as a gauge for future experiments, as well as to provide an estimate of the damage currents in actual ion implantation and plasma processing environments.

11:00am **PS-MoM9 Study of Synchrotron Radiation-Induced Surface-Conductivity of SiO@sub 2@ for Plasma Charging Applications***, **C. Cismaru**, J.L. Shohet,* University of Wisconsin, Madison*; J.P. McVittie,* Stanford University

During plasma processing, charging of dielectrics plays the leading role within the damage mechanisms. The charging potentials are determined by specific plasma and processed device parameters. Dielectric conductivity induced by vacuum ultraviolet (VUV) irradiation is one mechanism to affect dielectric charging not very well understood. In this work we investigate electrical surface conductivity in SiO@sub 2@ exposed to monochromatic synchrotron radiation for plasma charging applications. Special test structures were exposed to controlled fluxes of monochromatic synchrotron radiation in the range of 500 Å to 3000 Å (approx. 4 eV to 25 eV), the energy band of most plasma VUV radiation, at the Synchrotron Radiation Center, University of Wisconsin-Madison. During the exposure, radiation-induced currents in SiO@sub 2@ were monitored while controlling the electric field across the sample. Results show different characteristics of the photoinduced currents depending on the intensity of the electric field, thickness of the oxide, and radiation wavelength. Implications of these results on plasma charging of dielectrics will be discussed. This work was supported in part by the National Science Foundation under Grant No. EEC 8721545 and the Semiconductor Research Corporation under Contract No. 98-1J-106. The Synchrotron Radiation Center is a national facility, funded by the National Science Foundation under Award No. DMR-9531009.

11:20am **PS-MoM10 Effect of Surface Oxide Loss on Surface Potential Measurement (SPM) Accuracy for Plasma Charging Damage Characterization***, **S. Ma**, K. Nauka, R. Kavari,* Hewlett-Packard Company

It is well recognized that the surface potential measurement (SPM) technique can be used as a process diagnostic tool for evaluating plasma-induced charging damage in MOS devices. To date, it is the simplest and cheapest non-invasive method using blank oxide wafers to monitor cumulative wafer charging after plasma exposure. Despite of its convenience, SPM's results do not always correlate well with MOS device charging damage data, especially in sputter clean, metal etch and oxide etch processes. There is limited understanding currently available to explain why the weak correlation sometimes exists. This paper examines the reason why surface potential measurement (SPM) results after plasma exposure do not always correlate to the results of plasma induced charging damage measurement on devices. One very important explanation has been found to be non-uniform surface oxide loss during plasma exposure on test wafers. From biased oxygen plasma exposure experiments in a M0RI source high density plasma etcher, the SPM results lost their correlation to antenna capacitor device damage when the substrate bias was sufficient to etch the surface oxide. As the amount of surface oxide loss increases, deposited surface charge distribution correlates better to surface oxide loss than to the damaged antenna capacitor data. Longer plasma exposure time with more oxide loss also shifts the SPM results to a higher averaged value. Compared to the device damage data, the critical surface oxide loss causing misleading SPM results is estimated to be around 70Å. Therefore, this characterization method is applicable to plasma induced charging damage for limited processes that do not cause severe surface oxide loss such as resist ashing, high oxide selectivity poly etch, etc.

Surface Science Division

Room 606 - Session SS1+EM-MoM

Chemistry on Oxides

Moderator: S.A. Joyce, Pacific Northwest Laboratory

8:20am **SS1+EM-MoM1 The Reactions of Maleic Anhydride Over TiO@sub 2@ (001) Single Crystal Surfaces*, J.N. Wilson*,** *D.J. Titheridge, H. Idriss,* The University of Auckland, New Zealand

The reactions of maleic anhydride have been investigated on the stoichiometric and substoichiometric surfaces of TiO@sub 2@ by Temperature Programmed Desorption (TPD) and Scanning Kinetic Spectroscopy (SKS). SKS technique, showing complementary information to TPD, has been successfully applied to investigate the chemical pathways on this oxide material for the first time. Results from the maleic anhydride TPD and SKS show the desorption of a wide variety of products in several temperature domains. In addition to the decomposition pathway to CO, CO@sub 2@, acetylene, and ethylene, the desorption of coupling reaction products of two molecules of acetylene to vinylacetylene (m/e 52) and of three molecules of acetylene to benzene (m/e 78) is observed. Moreover, the potential desorption of carbon suboxide, O=C=C=C=O, formed by two successive dehydration of both ends of the molecule, is discussed. The coupling pathways of the reactions of maleic anhydride on the substoichiometric surface were more accentuated.

8:40am **SS1+EM-MoM2 S Adsorption on TiO@sub 2@(110) Studied with STM, XPS and LEED*, E.L.D. Hebenstreit*,** *W. Hebenstreit, U. Diebold,* Tulane University

TiO@sub 2@ surfaces are well-known for their catalytic properties. Since sulfur is known as a catalyst inhibitor, its adsorption behavior on TiO@sub 2@ single crystal surfaces are of great interest. Measurements with a scanning tunneling microscope reveal the existence of two different adsorption sites, depending on the sample temperature during adsorption. Adsorption at room temperature leads to very mobile sulfur atoms sitting on titanium sites of TiO@sub 2@(110). Adsorption at 300°C causes the formation of more stable sulfur chains running along the [1-10] direction with an ordered (3x1) structure at saturation. In the latter case the sulfur atoms are located at the positions of oxygen surface atoms. X-ray-photoelectron-spectroscopy confirms the existence of two chemically different S species.

9:00am **SS1+EM-MoM3 Spectroscopic Studies of Sorption Processes at Metal Oxide-Aqueous Solutions Interfaces*, G.E. Brown, Jr.*,** *T. Kendelewicz,* Stanford U.*; P. Liu,* LBNL*; J.R. Bargar,* Stanford Synchrotron Radiation Lab.*; J.P. Fitts, A.L. Foster, J.D. Ostergren, G.A. Parks, A.H. Templeton,* Stanford U.*; H.A. Thompson,* LANL*; S.N. Towle,* Intel Corp.*; T.P. Trainor,* Stanford U.*; P. Eng, S. Sutton,* Adv. Photon Source **INVITED**

Chemical interactions at metal oxide-aqueous solution interfaces are of great significance in atmospheric and environmental chemistry. They help control many important processes including dissolution and crystal growth of natural solids and the sorption a nd desorption of aqueous metal ions, which can sequester or release heavy metal contaminants in atmospheric and aquatic environments. Metal oxide-water interfaces in natural systems are extremely complex when viewed at the molecular level because of the many variable that must be accounted for and the difficulty in observing the products of interfacial reactions under in-situ conditions (i.e., with bulk water present). To make this problem more tractable, we have employed a reductionist approach in which interfacial reaction products are examined in simplified model systems under carefully controlled conditions using a combination of classical surface chemistry methods, synchrotron radiation-based surface science methods, and other spectroscopic and scanning force microscopy methods. The resulting information at macroscopic and atomic/molecular scales allows sorption behavior to be correlated with chemical species information, including the structure, composition, and mode of sorption of adsorbates, and, in selected cases, the types of reactive sites on adsorbent surfaces and the effect of aging time. In parallel model system studies, we have also examined the effects of common inorganic ligands, organic ligands, and biofilms on the sorption of metal ions at mineral-water interfaces, and we have used the results as a basis for studies of As and Pb speciation in contaminated soils and mine tailings. These studies have revealed the structure and composition of adsorbates, and for single-crystal adsorbents, have allowed us to place constraints on the stoichiometry of sorption reactions, including the types of reactive sites to which the adsorbate binds. Selected examples of these studies will be presented.

9:40am **SS1+EM-MoM5 Reactions of SeF@sub6@ with Iron and Iron Oxides*, S.R. Qiu*[1],** *H.-F. Lai, H.T. Than, C. Amrhein, J.A. Yarmoff,* University of California, Riverside

Concentrated levels of selenium in the groundwater of the western US have been found to cause the death and birth-deformation of wildlife. Zero valent iron has been used to immobilize many soluble toxic groundwater contaminants, including selenate (Se@super6+@), by a surface redox reaction in which aqueous contaminants are reduced to less mobile forms. Only limited success has been achieved in the field, however, as the understanding of the reaction mechanism at the liquid/solid interface is incomplete. In this work, the remediation process is modeled by the reaction of SeF@sub6@ with iron and iron oxide surfaces in ultra-high vacuum. Se in SeF@sub6@ is in the same oxidation state as in selenate, and a similar reduction is observed upon reaction with Fe. X-ray photoelectron spectroscopy (XPS) spectra collected following the exposure of a sputter-cleaned Fe foil to SeF@sub6@ show both Se and F on the surface. The Se is found to be directly bonded to Fe, with no bonds to F remaining, indicative of the complete dissociation of SeF@sub6@. The F-to-Se ratio is close to 6 to 1, showing that all of the products remain on the surface. The Fe 2p spectra show the formation of FeF@sub2@ as the major surface species formed. These results suggest that there is a high activation barrier to adsorption, but that once it occurs, the excess energy liberated by the exothermic reaction promotes complete dissociation. To ascertain the role of oxygen, SeF@sub6@ was exposed to both partially and fully oxidized Fe surfaces. Oxygen was found, in all cases, to inhibit the reaction. We are currently investigating this reaction employing clean and oxygen pre-covered single crystal Fe surfaces. Both XPS and scanning tunneling microscopy are being used to understand the chemical reaction mechanism and to ascertain the adsorption sites. The implications of our results on practical remediation methods will be discussed.

10:00am **SS1+EM-MoM6 Interactions of HCOOH with Stoichiometric and Defective SrTiO@sub 3@(100) Surfaces*, L. Wang*,** *F. Ferris, H. Engelhardt,* Pacific Northwest National Laboratories

Interactions of HCOOH with stoichiometric (nearly defect-free) and defective SrTiO@sub 3@(100) surfaces have been studied using x-ray photoelectron spectroscopy (XPS), temperature programmed desorption (TPD), and electronic structure calculations. Two reaction pathways were observed for formaldehyde formation from formic acid on SrTiO@sub 3@(100) surfaces. On stoichiometric surfaces, formaldehyde was produced through bimolecular coupling of two formates. However, on Ar+ sputtered surfaces, formaldehyde formation involves the reduction of surface formate by the oxidation of reduced Ti cations. XPS results show that surface defects on sputtered SrTiO@sub 3@(100) surfaces were reoxidized significantly upon exposure to 30 L HCOOH at 300 K, in contrast to defects on sputtered TiO@sub 2@(110) surfaces where no reduction in defect intensity was observed under the same condition. The fact that surface formate was reduced at 300 K on SrTiO@sub 3@(100) is clearly evident in TPD data where the desorption peak of formaldehyde is shifted to a lower temperature and broadened significantly down to 300 K for Ar+ sputtered SrTiO@sub 3@(100) surfaces as compared with stoichiometric surfaces. Electronic structure calculations have been used to investigate the

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

adsorptive interactions for formate and formaldehyde on the cation sites of both stoichiometric and defective SrTiO@sub 3@(100) surfaces. The results for formate indicate a strong adsorptive interaction consistent with the experimental observations, with significant charge redistribution. Further results will be discussed in terms of potential reaction mechanisms.

10:20am **SS1+EM-MoM7 The Structure of the CeO@sub 2@(001) Surface and its Reactions with D@sub 2@O***, G.S. Herman,* Pacific Northwest National Laboratory*; Y.-J. Kim,* Taejon National University of Technology, Korea*; S.A. Chambers, **C.H.F. Peden,*** Pacific Northwest National Laboratory

Angle-resolved mass-spectroscopy of recoiled ions (AR-MSRI) has been used to determine the surface structure of CeO@sub 2@(001). The results indicate that the surface is terminated with 0.5 monolayers of oxygen which gives rise to a zero dipole moment and, thus, a stable surface. The interaction of D@sub 2@O with the CeO@sub 2@(001) surface was studied with temperature programmed desorption (TPD) and x-ray photoelectron spectroscopy (XPS). It was found with TPD that D@sub 2@O desorption occurs in three states with temperatures of 152, 200, and 275 K which are defined as multilayer D@sub 2@O, weakly bound surface D@sub 2@O, and hydroxyl recombination, respectively. O 1s XPS measurements for high D@sub 2@O exposures, where multilayer water desorption was observed in the TPD, resulted in emission from only the substrate and surface hydroxyls. This is likely due to a non-wetting behavior of D@sub 2@O on this surface with the formation of nanosized clusters. An analysis of the O1s XPS data indicates that the surface has a hydroxyl coverage of 0.9 monolayers for large water exposures at 85 K. This is consistent with a model in which the polar CeO@sub 2@(001) surface can be stabilized by a reduction of the dipole in the top layer by the formation of full monolayer of hydroxyls. @FootnoteText@ 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.

10:40am **SS1+EM-MoM8 The Correlation Between MgO (100) Surface Morphology and Chemical Reactivity***, **S.S. Perry,*** University of Houston, US*; S. Imaduddin, O. El-bjeirami, P.B. Merrill, S.M. Lee, H.I. Kim,* University of Houston

A critical ingredient of any surface science study is the preparation of the surface so as to present a uniform and homogeneous distribution of surface sites. For metals, the nature of adsorption site is determined by the crystal face exposed and the local coordination of the different metal atoms at the surface. For compound semiconductors and oxide based materials, the situation can be much more complex as the crystal face and coordination now applies to more than one type of element. The preparation of such materials can be further complicated by the possibility of preferential sputtering of one component of the surface. In this study we have used a combination of microscopy, ex-situ processing, ultrahigh vacuum (UHV) processing and UHV surface analysis to correlate the chemical reactivity of a model metal oxide (MgO) with the nature of surface structure and morphology. Atomic force microscopy, low energy electron diffraction, and reflection high energy electron diffraction studies together have allowed the distinction between amorphous and crystalline surfaces as well as the length scale of surface order. Single crystal MgO(100) surfaces have been prepared by a number of procedures including acid etching, high temperature annealing in ambient pressures of oxygen, UHV annealing, and ion bombardment. The compositional changes of the surface region with respect to these procedures have been followed with X-ray photoelectron spectroscopy. Finally, the chemical reactivity of the MgO(100) surface has been studied using temperature programmed desorption, investigating the desorption properties of water, methanol and carbon monoxide. Together, these studies have generated a complete picture of the relationship between microscopic surface morphology and chemical reactivity for this model metal oxide surface and have highlighted several critical aspects involved in the preparation of single crystal metal oxide surfaces for UHV surface science studies.

11:00am **SS1+EM-MoM9 Photoconversion of Adsorbed Oxygen States On TiO@sub 2@(110)***, **C.L. Perkins,** M.A. Henderson,* Pacific Northwest National Laboratory

By means of postirradiation temperature programmed desorption we have investigated further the states of oxygen adsorbed on rutile TiO@sub 2@. Previous work has shown that annealing the (110) surface in vacuum produces isolated bridging oxygen vacancies, and that these vacancies are intimately connected with molecular and dissociative oxygen adsorption channels. We find that at 120 K illumination of the oxygen exposed surface with photons having energies above the band gap (>3.6 eV) results in depletion of the molecular oxygen state observed at 410 K in TPD, in contrast to the remaining oxygen destined for the dissociative channel. An unusual effect of water overlayers on the O/TiO@sub 2@(110) system is explored. For thick overlayers (> 2 ML), it is possible to generate via UV irradiation a previously unobserved oxygen TPD state. Cross sections for the photoconversion of oxygen into this state are measured, and specific mechanisms for the process are proposed.

11:20am **SS1+EM-MoM10 Reactions of Acetic Acid, Acetaldehyde and Ethanol on the (111) Surface of Uranium Dioxide Single Crystal***, S.V. Chong, **H. Idriss,*** The University of Auckland, New Zealand

The reactions of three C2 molecules having different functional group and polarity, have been investigated on the (111) surface of uranium dioxide single crystal, which has been characterised by LEED and AES. The adsorption of acetic acid, the most polar among the three molecules, indicates a higher sticking probability on the oxygen terminated UO@sub 2@(111) surface, followed by ethanol then acetaldehyde. Temperature Programmed Desorption (TPD) for these molecules displays a rich chemistry. Acetic acid-TPD on a stoichiometric surface yields ketene (dehydration) as the main product, plus acetaldehyde (reduction) as the minor product. While on an electron beam sputtered surface, two additional products were observed - butene and crotonaldehyde. In the case of acetaldehyde, both sputtered and non-sputtered surfaces yield benzene, with ketene as the additional product on the sputtered surface. The reactions of ethanol on a stoichiometric surface give acetaldehyde and ethylene as the only two products with "equal" amount. The comparison of this latter result with those of other metal oxide single crystals indicates a plausible relationship between the dehydrogenation/dehydration selectivity of primary alcohols and the Madelung potential of the cations. In summary, this investigation has shown the ability of UO@sub 2@(111) single crystal to oxidise, reduce, reductively couple, and trimerise organic molecules.

11:40am **SS1+EM-MoM11 Surface Reactions on Cr-doped V@sub 2@O@sub 3@***, **D.S. Toledano,** V.E. Henrich,* Yale University

Transition-metal oxides are important as gas sensors due to chemisorption-induced changes in surface conductivity. Conversely, changes in substrate electronic structure may alter surface chemisorption properties. While investigating the effect of metal-insulator transitions in Cr-doped V@sub 2@O@sub 3@ on adsorption, we have observed interesting effects involving surface reduction by CO, as well as differences in adsorption on metallic and insulating substrate phases. (Cr@sub 0.015@V@sub 0.985@)@sub 2@O@sub 3@ exhibits two metal-insulator transitions as a function of temperature; these experiments focus on the insulating phase of single-crystal Cr-V@sub 2@O@sub 3@ using UPS, XPS, LEED and AES. When insulating-phase Cr-V@sub 2@O@sub 3@ (0001) is exposed to CO at 273K, CO appears to adsorb dissociatively up to 10@super 3@ Langmuir. Higher exposures result in a C-containing species, and electron transfer to V cations at energies near E@sub F@; decreased occupation of non-bonding O orbitals is also observed. Heating to 470K desorbs this species, but the surface is further reduced after desorption, with increased charge transfer to V cations. Exposure of a CO-reduced surface to O@sub 2@ does not reoxidize the surface or restore the original electronic structure, but appears to result in adsorbed O@super -@ or (O@sub2@)@super -@ which does not re-enter the lattice unless annealed above 700K. CO adsorption on metallic-phase Cr-V@sub 2@O@sub 3@ differs from that on the insulating phase for intermediate exposures, exhibiting higher initial sticking coefficient and desorption temperature; however, the two phases behave similarly for high CO exposures. Adsorption of H@sub 2@O, SO@sub 2@ and O@sub 2@ on both substrate phases has also been studied. This work was partially funded by NSF grant CTS-96-10140

Surface Science Division
Room 607 - Session SS2-MoM
Catalysis on Metals

Moderator: J.W. Niemantsverdriet, Eindhoven University of Technology, The Netherlands

8:20am **SS2-MoM1 The Influence of a Catalytic Surface on the Gas Phase Ignition and Combustion of H2+O2***, **M. Försth,** F. Gudmundson, J. Persson, A. Rosén,* Chalmers University of Technology, Sweden

The OH concentration outside a Pt catalyst at 1300K, in a stagnation flow of 90% O@sub 2@ and 10% H@sub 2@, has been studied by Planar Laser Induced Fluorescence, PLIF, and compared to measurements outside a heated glass surface. The total pressure in the system was varied from 0.2 to 120 torr. At low pressure, surface reactions were observed for the Pt surface, but not for the glass. At higher pressure, gas-phase ignition occurred for both systems, but not at the same pressure: ignition occurred at a lower pressure outside the inert glass surface. Computer modeling using CHEMKIN confirmed these results. The difference in gas-phase ignition is also seen in the modelling results, and it is due to the removal of atomic O and H from the gas by adsorption and reaction on the catalytic surface. The catalytic reaction mechanism on the surface plays an important role as it enhances the removal of radicals, compared to a surface where only radical recombination back to reactants is allowed.

8:40am **SS2-MoM2 Catalytic Oxidation of Unsaturated C@sub 3@ Hydrocarbons on the Pt (111) Surface**, ***A.M. Gabelnick***, *A.T. Capitano, D.J. Burnett,* University of Michigan; *D.A. Fischer,* National Institute of Standards and Technology; *J.L. Gland,* University of Michigan

The catalytic oxidation of unsaturated C3 hydrocarbons (propylene and methylacetylene) has been studied in-situ in oxygen pressures ranging from UHV to 0.01 torr on the Pt(111) surface. Using a combination of kinetic and spectroscopic in-situ fluorescence yield soft X-ray techniques, we have characterized the oxidation of these hydrocarbons based on absolute carbon coverage and identified oxidation intermediates spectroscopically. The adsorbed intermediates for oxidation of preadsorbed propylene, propylene catalytic oxidation (both propylene and oxygen in the gas phase), and methylacetylene oxidation have been characterized. Despite differences in these intermediates, skeletal oxidation begins at the same temperature, indicating a common rate limiting step in the oxidation process. In the catalytic oxidation of propylene, dehydrogenation of propylene occurs prior to skeletal oxidation, even with both propylene and oxygen in the gas phase. In pressures of oxygen, a monolayer of propylene and methylacetylene completely oxidize by 450 K, with skeletal oxidation of both hydrocarbons beginning near 320 K. Quantitative kinetic studies of methylacetylene oxidation over a range of conditions enabled the determination of both the activation energy and order of the reaction in oxygen. Experiments performed with coadsorbed oxygen confirm that O(a) is the oxidizing agent.

9:00am **SS2-MoM3 Thermal Conversion of C@sub 3@ Fragments on Pt(111): Evidence for the Formation of Allylic Intermediates**, *D. Chrysostomou, C.R. French, J.M. Guevremont,* ***F. Zaera***, University of California, Riverside

Platinacyclobutane was selectively formed on Pt(111) via the thermal activation of adsorbed 1,3-diiodopropane, and the mechanism for its conversion to propene was investigated using temperature programmed desorption (TPD) and reflection absorption infrared spectroscopy (RAIRS). Thermal desorption of propene from 1,3-diiodopropane occurs at 370 K. The conversion is suggested to involve the formation of a surface bound allylic intermediate. Allyl iodide was used to investigate the further reactivity of that intermediate, and additional experiments were carried out with propyl iodide and propylene as well. Selective deuteration of 1,3-diiodopropane was explored as a mean to determine the C'H bonds active in the metallacycle to propene conversion, but the usefulness of this approach was limited by extensive scrambling in platinacyclobutane prior to the formation of propene. Propene itself was identified to exist on the surface in three different configurations depending on the coverage: di-sigma bonded, pi bonded, and weakly physisorbed. The results from this work provide new insights into the mechanism of hydrocarbon reforming reactions.

9:20am **SS2-MoM4 Reactions of Methyl Groups on Sn/Pt(111) Alloys**, ***B.E. Koel***, *H. He,* University of Southern California

Reactions of alkyl intermediates are important in many catalytic hydrocarbon reactions over metal and metal alloy surfaces. Reactions of adsorbed CH@sub 3@ (methyl) groups, formed using a pyrolytic azomethane source to produce incident methyl radicals, on two ordered Sn/Pt(111) surface alloys have been studied using HREELS, UPS, TPD, AES and XPS. Chemisorbed CH@sub 3@ species are identified at low doses but longer chain hydrocarbons can be formed at high doses on both Sn/Pt(111) surfaces at 100 K. Chemisorbed methyl groups are characterized by a prominent peak in UPS at 8 eV BE (CH@sub 3@ HOMO) and a strong peak in HREELS at 1240 cm@super -1@ from the @delta@@sub s@(CH@sub 3@) mode. These studies show that alloyed Sn decreases the dehydrogenation rates of akyl groups on Pt(111) surfaces and enables other C-C bond coupling reactions to occur. Alkane and alkene products were desorbed below 200 K in TPD for both Sn/Pt(111) surface alloys. On the (2x2) alloy, only CH species are stable at 300 K, and these react to desorb CH@sub 4@ at 432 K. TPD after methyl dosing on the (@sr@3x@sr@3)R30° alloy at 300 K gave only one very sharp CH@sub 4@ desorption peak at 453 K, and we propose that this arises from decomposition of CH@sub 3@CH species. The chemistry of Pt-Sn alloy surfaces leads to much lower carbon buildup than on Pt surfaces from thermal reactions of alkyl adsorbates.

9:40am **SS2-MoM5 Mechanisms and Dynamics in Millisecond Chemical Reactors**, ***L.D. Schmidt***, University of Minnesota **INVITED**

It is possible to carry out the partial oxidation of alkanes in reactors with residence times less than 10@super -3@ sec above atmospheric pressure and obtain almost complete conversions with high selectivities to products such as H@sub 2@ and CO, olefins, and oxygenated hydrocarbons. These processes involve extremely large temperature and concentration gradients (10@super 6@ K/sec and 10@super 4@ atm/sec), and at temperatures above 1300K where adsorption lifetimes are typically 10@super -9@ sec. For the oxidation of ethane to ethylene, we can obtain 85% selectivity to ethylene with less than 5% CO and CO@sub 2@, even though at equilibrium CO should be the dominant product. These reactions occur on a PtSn catalyst surface which consists of ~10 µm single crystal particles exposing large facets. EDX and XRD of these catalysts show that they consist entirely of intermetallic PtSn compounds with no free Pt phases. This is accomplished by adding large amounts of H@sub 2@ in a ratio of H@sub 2@/O@sub 2@=2. With this feed, the surface reaction forming H@sub 2@O occurs within the first 100 µsec on the first mm of catalyst, while minimizing ethane oxidation. This consumes all O@sub 2@ leaving ethane dehydrogenation which generates as much H@sub 2@ as is fed to the reactor. At 1300K with 10@super -9@ sec adsorption times and very high reactive fluxes, these processes deviate considerably from conventional catalytic reaction conditions, and these processes may involve partially equilibrated internal states of molecules. Implications of nonequilibrium reaction dynamics at extreme these conditions will be considered.

10:20am **SS2-MoM7 In-situ Studies of C-C Hydrogenolysis in Cyclopropane on Platinum using a Combination of Soft X-ray Methods**, *A.T. Capitano, A.M. Gabelnick,* University of Michigan; *D.A. Fischer,* National Institute of Standards and Technology; ***J.L. Gland***, University of Michigan

In-situ studies fluorescence soft X-ray studies clearly show that a propyl intermediate plays an important role during cyclopropane hydrogenolysis to form propane over the Pt(111) surface. Through a combination of spectroscopic and in-situ catalytic studies, a complete picture of hydrogen induced C-C bond breaking mechanisms during cyclopropane hydrogenolysis has been developed. Molecular cyclopropane is adsorbed in a tilted configuration and desorbs in the 130 K temperature range. Preadsorbed cyclopropane desorbs before reacting with hydrogen, even for pressures as high as 0.02 torr. When both cyclopropane and hydrogen are present in the gas-phase, propane is formed above 300 K. In this temperature range, in-situ soft X-ray studies of the adsorbed species show that a propyl intermediate is formed. The coverage and stoichiometry of this intermediate has been characterized over a range of temperatures and reactant ratios. For large excesses of hydrogen, the average hydrogen stoichiometry of the adsorbed species increases with increasing temperature while the amount of carbon remains constant. Characterization of the dominant intermediate at 300 K with FY-NEXAFS indicates that the hydrogenated intermediate is an adsorbed propyl species. Detailed isothermal kinetic studies were used to establish both the activation energy and prefactor for hydrogenation of this intermediate. During in-situ catalytic studies, an additional C@sub 3@ adsorbed species is observed in the 150 K temperature range. By using FY-NEXAFS, the structure and bonding of this intermediate has been characterized and is consistent with adsorbed cyclopropyl-like. These exciting results have clearly established for the first time under catalytic conditions that C-C bond breaking in cyclopropane proceeds via sequential hydrogen addition.

10:40am **SS2-MoM8 Direct Evidence of Surface Intermediates from the Reactions of C@sub 3@ Hydrocarbons on Cu(100)**, ***H. Celio***, *K.C. Smith, J.M. White,* University of Texas, Austin

Using reflection absorption infrared spectroscopy (RAIRS) and temperature programmed desorption (TPD), we have characterized important intermediates of the thermal and electron-induced surface chemistry of C3 hydrocarbons on Cu(100). The molecules that have been studied include allyl bromide, allyl chloride, propene, and cyclopropane. We find that the allyl halides dissociate to form pi-bonded allyl groups and halogen atomns at a wide temperature range (110-350 K). Furthermore, we observed an exceptionally facile carbon-carbon coupling between allyl bromide and pi-bonded allyl groups that lead to the formation of 1,5-hexadiene at 110 K. Conversely, allyl chloride principally forms pi-bonded allyl groups, which remained inert in the presence of allyl chloride molecules on the second layer. The implications of the dissimilar surface reactions of these allyl halides are discussed in terms of an Eley-Rideal rather than a diffusion-limited reaction. Electron irradiation (<50 eV) of weakly adsorbed cyclopropane lead to the formation of metallacyclobutane and cyclopropyl groups at 100 K. The thermal chemistry of the latter products yield propene but not pi-bonded allyl groups. The results of the allyl halides and cyclopropane are also compared and discussed for Ag(111).

11:00am **SS2-MoM9 Carbon-Carbon Coupling from Formaldehyde Reaction on Mo(110)***, K.T. Queeney,* Harvard University*;* ***C.R. Arumainayagam,*** Wellesley College*; C.M. Friend,* Harvard University

Formaldehyde (CH@sub 2@O) reaction on Mo(110) was studied with temperature programmed reaction and infrared reflectance absorbance spectroscopy. We present preliminary results which demonstrate the evolution of gas-phase ethylene from the formaldehyde reaction, to the best of our knowledge the first example of carbon-carbon bond formation on clean Mo(110). This reaction is proposed to proceed via an ethylene dialkoxide intermediate, analogous to that formed during reaction of ethylene glycol on Mo(110). Other reactions include hydrogenation of CH@sub 2@O to form a methoxy intermediate which subsequently undergoes C-O bond scission to evolve gas-phase methyl radicals at ~600 K.

11:20am **SS2-MoM10 Adsorption of Propylene Oxide on Pt(111) Surfaces and its Reactions with Gaseous and Adsorbed H Atoms***, A. Dinger, C. Lutterloh,* ***J. Biener****, J. Küppers,* Universität Bayreuth, Germany

The adsorption of propylene oxide (PO) on Pt(111) surfaces and its reactions with gaseous and adsorbed H atoms, respectively, was studied with TDS and HREELS methods. Monolayer PO desorbs near 180 K, while multilayer PO desorbs at 130 K. Approximately 50% of the monolayer PO molecules dissociate leading to the desorption of CO and H@sub 2@. The decomposition of PO is initiated by a cleavage of the C-O-C ring. Gas phase H atoms react with PO monolayers on Pt(111) to n-propanol, i-propanol, and acetone with the latter as a minor product and about equal amounts of the alcohols. On the other hand, the reaction between PO and coadsorbed hydrogen leads to the selective formation of acetone.

11:40am **SS2-MoM11 Interaction of Atomic Hydrogen and Deuterium with the Ir(111)-p(1x1)-H, Ir(111)-p(1x1)-D, and Ir(111)-p(1x2)-O Surfaces***,* ***C.J. Hagedorn****, M.J. Weiss, W.H. Weinberg,* University of California, Santa Barbara

The interaction of gas phase atomic hydrogen and deuterium with chemically modified Ir(111)-p(1x1)-D, Ir(111)-p(1x1)-H, and Ir(111)-p(1x2)-O surfaces at cryogenic temperatures has been studied using thermal desorption mass spectrometry and high-resolution electron energy loss spectroscopy. Although the Ir(111)-p(1x2)-O surface at a temperature of 90 K is passivated with respect to exposure to gas phase H@sub 2@ and D@sub 2@, the interaction of gas phase atomic H and D with this surface at 90 K results in the subsequent desorption of water in thermal desorption spectra. These results suggest that the dissociative chemisorption of molecular hydrogen on Ir(111) is precluded by the presence of the (1x2)-O oxygen overlayer, whereas energetically "hot" gas phase atomic hydrogen reacts readily with this oxygen modified surface. Moreover, a strong isotope effect has been observed in the interaction of gas phase atomic H and D with deuterium and hydrogen modified surfaces. The abstraction cross section for atomic D interacting with the Ir(111)-p(1x1)-H surface to form HD is approximately a factor of two greater than that for atomic H interacting with the Ir(111)-p(1x1)-D surface. This difference between the abstraction cross sections can be explained qualitatively by considering the differences associated with the expected zero point energy of the transition state for the abstraction reaction and the differences associated with the zero point energy between H and D adatoms.

Surface Science Division
Room 612 - Session SS3-MoM
Water-Surface Interactions

Moderator: E.M. Stuve, University of Washington

8:20am **SS3-MoM1 Surface Chemistry of Organic Aerosols***,* ***G.B. Ellison,*** University of Colorado, Boulder **INVITED**

Organic aerosols are believed to be important cloud condensation nuclei in the earth's atmosphere. We suggest a chemical model for the composition, structure, and atmospheric processing of these organic aerosols. This model is stimulated by recent field measurements showing that organic compounds are a significant component of atmospheric aerosols. The proposed model organic aerosol is an "inverted micelle" consisting of an aqueous core that is encapsulated in an inert, hydrophobic organic monolayer. We propose a chemical mechanism by which the organic surface layer will be processed by reactions with atmospheric radicals. Surface reactions of the hydrocarbon film with atmospheric species such as OH, Cl, O3, and NO3 will transform the organic film. The net result is the transformation of an inert hydrophobic film to a reactive hydrophilic layer.

9:00am **SS3-MoM3 Water Adsorption Structures on Flat and Stepped Ru(0001)-Surfaces***, W. Hoffmann,* ***C. Benndorf****,* University of Hamburg, Germany

We investigated the structural influence of vicinal Ru(0001) surfaces to water adsorption and desorption kinetics. Flat Ru(0001) surfaces show a unique behavior in the difference of H@sub2@O and D@sub2@O desorption spectra - referred to as the isotope effect. In accordance with other authors we observed on Ru(0001) three desorption peaks for H@sub2@O denoted as C, A@sub2@ and A@sub1@ (C, 155 K / A@sub2@, 190 K / A@sub1@, 212 K).The isotope effect for D@sub2@O on Ru(0001) is characterized by a missing A@sub1@ peak. Isothermal desorption measurements were performed using @Delta@@phi@, in order to determine the different kinetics for H@sub2@O and D@sub2@O. Neither for D@sub2@O nor for H@sub2@O the desorption of the A@sub2@-state can be described by 1st order kinetics. Especially for the A@sub2@ peak of H@sub2@O we observed an initial range of 1st order kinetics followed by a strong deviation, which could be described by Avrami kinetics or lateral interactions.@footnote 1@ Stepped Ru surfaces were used for comparison and @Delta@@phi@ measurements were complemented by ARUPS measurements of H@sub2@O and D@sub2@O adsorption. Further we performed LEED structure calculations of the clean stepped hcp(0001)-surfaces using a spherical wave model approach and single scattering theory.@footnote 2@ In experiments the vicinal Ru(0001) surfaces show a triplet spot splitting due to the alternating step width with different atomic arrangements at the steps, in agreement with our calculations. Regarding the adsorption phenomena on low indexed stepped surfaces, the diffraction pattern do not show ordered structures of water molecules. Higher indexed surfaces allow to built ordered water super structures as observed for flat Ru(0001) surfaces.@footnote 3@ @FootnoteText@ @footnote 1@ W. Hoffmann, C. Benndorf, Surface Sci. 377-379 (1997) 681-686. @footnote 2@ W.P. Ellis and R.L. Schwoebel, Surface Sci. 11 (1968) 82-98. @footnote 3@ D. L. Doering and T. E. Madey, Surface Sci. 123 (1982) 305-337.

9:20am **SS3-MoM4 Kinetics of Water Uptake on a Hydrophobic Surface Studied by UHV-TPD***,* ***T.R. Linderoth,*** *P. Löfgren,* Chalmers University of Technology, Sweden*; V.P. Zhdanov,* Boreskov Institute of Catalysis, Russia*; B. Kasemo,* Chalmers University of Technology, Sweden

Thin water (ice) films are currently receiving much attention. The motivations are both intrinsic scientific interest and their importance in areas such as astrophysics, biology and atmospheric chemistry. As a model of water adsorption on a very hydrophobic surface, we have investigated the uptake of water onto an octane (C@sub 8@H@sub 18@) covered Pt(111) surface and compared the results with previous studies on hydrophilic clean Pt(111). Our adsorption experiments were executed at substrate temperatures (T) in the range 100-120 K. A water-doser provided precise control of dosage flux (F) and exposure time (t). The adsorbed amount of water (@theta@) was determined by thermal desorption spectroscopy (TDS). In contrast to the case of hydrophilic metal substrates, we find that the apparent sticking (condensation) coefficient is well below unity for adsorption on the octane film (typically <<1 ML is adsorbed for exposures up to 10 ML). Furthermore, the adsorbed amount of water at a given exposure is strongly dependent on dosage flux and substrate temperature, being larger for higher F or lower T. Qualitatively, these findings can be understood if the binding of a single water molecule to the octane surface is so weak that adsorbed, diffusing water molecules can re-desorb before they manage to nucleate with other adsorbed molecules or incorporate into already stable water islands. A quantitative treatment of the corresponding kinetic equations yields: @theta@(t)~F@sup 3@exp[(3E@sub d@-2E@sub a@)/k@sub B@T]t@sup 2@ (E@sub d@/E@sub a@ are activation energies for desorption/surface diffusion of water molecules). The experimental data agree well with the predicted time and temperature dependences: We find that @theta@~t@sup 2.3@ and from the Ahrrenius analysis 3E@sub d@-2E@sub a@=0.20 eV is obtained. The observed flux-dependence of @theta@~F@sup 0.6@ is not in agreement with the model, however. Further investigations of the system are currently being undertaken.

9:40am **SS3-MoM5 Soft-Landed Ion Study of a Liquid-Liquid-Solid Interface*, J.P. Cowin,*** *K. Wu, M.J. Iedema,* Pacific Northwest National Laboratory

Ion beams with energies of about 1 eV allow one to gently land, without damage, molecular ions important to aqueous/organic liquid chemistry. We have used these soft-landed ions to probe the transfer of hydronium ions from non-aqueous to organic media. Molecular beam epitaxy is used to create aqueous/organic interfaces with monolayer precision, and the motion of the ions is detected with a non-contact work function probe, in UHV environments. Amorphous vapor- deposited films become true liquids above their glass temperatures (135 for water, 85 K for methyl cyclohexane (MCH)). We find hydrating the hydronium strongly effects its ability to enter the organic phase. We also see strong non-linear electric field effects. When a "dry" 30 monolayer MCH film is ramped at 0.2 K/s, we find that the ions traverse a film at about 97 K, under their self-induced field on order of 6 volts/(10.2 nm). We then added water with the ions on top of the MCH film. The temperature for ion transport shifts linearly with added water to 100 K at 0.4 monolayer, and is constant at @DELTA@T of 3K from 0.4 to 1.0 monolayer. This is consistent with an increase of ion size due a large hydration "sphere" (or pancake) being dragged through the organic film. Above 1 monolayer of added water the temperature shifts as much as 15 K, and is consistent with the expected @DELTA@G difference for transferring a solvated ions from this nano-aqueous environment to the organic phase. At electric fields from 0.01 to 0.1 V/angstrom, we see considerable deviations from simple viscosity-based ion transport models.

10:00am **SS3-MoM6 The Molecular Volcano: Release of Trapped Volatile Gases by Amorphous Solid Water*, K.P. Stevenson,*** *Z. Dohnálek, G.A. Kimmel, R.S. Smith, B.D. Kay,* Pacific Northwest National Laboratory

The trapping and release of volatile gases by amorphous solid water (ASW) has important astrophysical implications, predominately for the adsorption of gases on icy planetary surfaces and the outgassing behavior of cometary bodies. A previous study involving ASW and CCl@sub 4@ introduced the concept of the molecular volcano,@footnote 1@ wherein the abrupt release of trapped CCl@sub 4@ was driven by the amorphous to crystalline ice phase transition. The mechanism for the release of gas was postulated to be the formation of connected pathways in the ASW film during the nucleation and growth of the crystalline ice. We have investigated the mechanisms for trapping and release of volatile gases by ASW using temperature programmed desorption (TPD) from N@sub 2@, O@sub 2@, and Ar adsorbed underneath thin ASW films. The TPD of physisorbed N@sub 2@ monolayers from the ASW surfaces was used to probe the crystalline ice surface fractions and surface area changes during crystallization of the ASW films. The isothermal desorption and TPD of N@sub 2@, O@sub 2@, and Ar deposited beneath thin ASW overlayers results in the desorption of the trapped gas at the onset of crystallization in the ASW. During crystallization, the trapped gas escapes in concert with a cracking of the ASW film as observed by a significant change in film surface area. For thicker ASW overlayers (~600 BL), the gas release is delayed until after the ASW film has crystallized. A comparison with the isothermal desorption of pure ASW films, reveals that the amorphous to crystalline ice phase transition kinetics are independent of the trapped gas in the ASW films. @FootnoteText@ *Pacific Northwest National Laboratory is operated for the Department of Energy by Battelle under Contract DE-AC06-76RLO 1830. @footnote 1@ R. S. Smith, C. Huang, E. K. L. Wong, and B. D. Kay, PRL, 79, (1997) 909.

10:20am **SS3-MoM7 The Effect of Water on the Nitric Acid Pressure Dependence of the Reaction Between Gas Phase Nitric Acid and NaCl Surfaces.@footnote 1@*, J.C. Hemminger,*** *S. Ghosal,* University of California, Irvine

The reactions of oxides of nitrogen with sea salt particles, that liberate halogenated compounds into the gas phase, may play an important role in the chemistry of the marine troposphere. Recent laboratory measurements have shown that the reactive sticking coefficient of HNO@sub 3@ on NaCl particles exhibits a significant dependence on the HNO@sub 3@ pressure, when the measurements are carried out under conditions of steady state reaction. This pressure dependence has been rationalized in terms of a two-site Langmuir model for dissociative adsorption of the HNO@sub 3@. However, our XPS experiments show that the dissociative adsorption of HNO@sub 3@(g) on NaCl to form NaNO@sub 3@(s) and HCl(g) follows single-site Langmuir adsorption behavior. We also used XPS to show that the amount of "strongly adsorbed water" on the surfaces of NaCl particles strongly depends on the particle size. Particles of 1-10 micron diameter show large quantities of adsorbed water that remain on the sample up to temperatures of 200 degrees C. Particles in the size range of 500 micron diameter have less, but still easily measurable, amounts of strongly adsorbed water. We present a model for the HNO@sub 3@ pressure dependence of the reactive sticking coefficient of HNO@sub 3@ on NaCl under steady state reaction conditions. The origin of the pressure dependence in the model is the competition between site blocking on the surface by the build-up of the NaNO@sub 3@ reaction product and the water induced 3-d recrystallization of the NaNO@sub 3@ that frees up reactive sites for further reaction. @FootnoteText@ @footnote 1@ This work was supported by the National Science Foundation Grant ATM-9707285.

10:40am **SS3-MoM8 Giant Cl@super-@ and F@super-@ Enhancements in Electron-Stimulated Desorption of CF@sub2@Cl@sub2@ Coadsorbed with Water or Ammonia Ices: Implications for Atmospheric Ozone Depletion*, T.E. Madey,*** *Q.-B. Lu,* Rutgers, The State University of New Jersey

Dissociative electron attachment to form Cl@super-@ and F@super-@ can be an important process for the destruction of ozone-depleting chlorofluorocarbons (CFCs) in the upper atmosphere, because of their extremely large electron attachment cross sections.We have observed giant Cl@super-@ and F@super-@ enhancements by several orders of magnitude in electron-stimulated desorption of a fractional monolayer of CF@sub2@Cl@sub2@ coadsorbed with water ice and ammonia ice on a Ru(0001) surface at ~25 K, respectively. The yields of negative ions are measured by an electron-stimulated-desorption ion angular distribution (ESDIAD) detector with time-of-flight capability. The enhancement of Cl@super-@ is much stronger than that of F@super-@, and the enhancements for both ion species by NH@sub3@ coadsorbate are stronger than by H@sub2@O. Moreover, all magnitudes of enhancement increase strongly with decreasing CF@sub2@Cl@sub2@ concentration; for 0.3 ML CF@sub2@Cl@sub2@, the largest Cl@super-@ enhancements are ~3x10@super4@ for NH@sub3@ and ~10@super2@ for H@sub2@O. In contrast, the enhancements are much smaller for CF@sub2@Cl@sub2@ coadsorption with rare-gas atoms or nonpolar molecules. Whereas the primary electron beam energy is 250 eV, the giant negative-ion enhancements are attributed to dissociation of CF@sub2@Cl@sub2@ by capture of low-energy secondary electrons self-trapped (solvated) in polar water or ammonia clusters. This process may be an important sink for chlorofluorocarbons (CFCs) in the atmosphere, where low-energy electrons created by cosmic ray ionization can be trapped in clouds. Cl@super-@ ions produced may be directly or indirectly converted to Cl atoms, which then destroy ozone.

11:00am **SS3-MoM9 Cation Trapping Effects on HCl Diffusion in Ice Measured Using a New Laser Resonant Desorption Depth-Profiling Technique*, F.E. Livingston,*** *S.M. George,* University of Colorado, Boulder

HCl diffusion in ice is important for an understanding of heterogeneous atmospheric chemistry on ice particles and may influence the interpretation of ice core data. The diffusion of alkali metals in ice is also relevant for the evaluation of ice core samples and alkali cations may interact strongly with coadsorbates in ice. Novel laser resonant desorption depth-profiling techniques were used to measure HCl and Na diffusion in ice. The diffusion was monitored using a Q-switched Er:YAG laser to depth-profile the ice multilayer. The Er:YAG laser emits infrared light at 2.94 microns. This light can be resonantly absorbed by the O-H stretching vibration of H@sub2@O and thermalized to induce resonant desorption. HCl diffusion was monitored in ice multilayers containing a thin HCl interlayer. The HCl spatial coverages at various diffusion times and temperatures were used to extract the diffusion coefficients. The measured HCl diffusion coefficients ranged from D=(3.8±2.8)x10@super-13@ cm@super2@/s at T=169 K to D=(2.0±1.5)x10@super-10@ cm@super2@/s at T=197 K. Arrhenius analysis yielded diffusion kinetic parameters of E=14.6±1.6 kcal/mol and D@subo@=(2.9±2.0)x10@super6@ cm@super2@/s. Na was also observed to diffuse in the ice multilayers. In addition, coadsorbed Na decreased the HCl diffusion rate by a factor of ~5-85 for Na/Cl ratios ranging from 0.05-0.5. The Na-induced decrease in the HCl diffusion rate may be attributed to cation trapping manifested by NaCl formation in the ice.

11:20am **SS3-MoM10 The Effect of Porosity on the Crystallization of Amorphous Solid Water***, **Z. Dohnálek**, G.A. Kimmel, K.P. Stevenson, R.S. Smith, B.D. Kay,* Pacific Northwest National Laboratory

The annealing and crystallization of amorphous solid water (ASW) is important to understand the properties of ice in extraterrestrial environments. Here we show a dramatic effect of the initial porosity of the ASW films on their crystallization kinetics. The porosity of the films was varied by changing the incident angle of the H@sub 2@O molecules during the deposition.@footnote 1@ The crystallization kinetics were followed using the temperature programmed desorption (TPD) of N@sub 2@(g) monolayers from the ASW film surface. Despite the fact that the films densify upon annealing, before any crystallization takes place, a strong dependence of the crystallization kinetics on the initial porosity exists. The crystallization of dense ASW films (grown at zero angle of incidence) proceeds via classical bulk nucleation and 3-dimensional growth. In the case of porous films (grown at high angles of incidence) the crystallization half time is reduced by more than an order of magnitude and the apparent activation energy decreases to a value that corresponds to the growth of the crystalline phase in the absence of nucleation. We propose that the lowering of the activation energy is due to seeding of the porous films that is likely to occur during the densification. This conclusion is supported by detailed Monte Carlo simulations of the effect of seeding on the crystallization kinetics. @FootnoteText@ * Pacific Northwest National Laboratory is operated for the Department of Energy by Battelle under Contract DE-AC06-76RLO 1830. @footnote 1@ K. P. Stevenson, G. A. Kimmel, Z. Dohnálek, R. S. Smith, and B. D. Kay, Science 283 (1999) 1505.

Thin Films Division
Room 620 - Session TF+VM-MoM

Advances in Hard and Superhard Coatings I

Moderator: F. Sequeda, Universidad del Valle, Columbia

8:20am **TF+VM-MoM1 Advances in Hard and Superhard Coatings for Tribological Applications***, **A. Matthews**, A. Leyland,* University of Hull, UK **INVITED**

Over the past twenty years there has been considerable progress both in the development of advanced coating processes and in the scientific understanding of tribological mechanisms. Typically these developments have occurred completely separately, to the extent that coatings researchers may seek to develop a new coating with a specific extreme property (such as high hardness) driven primarily by scientific curiosity, rather than a desire to fulfil an identified tribological need. Usually that need will (for example) require an enhanced range of properties (such as hardness, toughness and resistance to environmental degradation). Coatings researchers are now increasingly recognising this need and are fulfilling it through several exciting developments. These include multi-layered and nanocomposite coatings which combine high hardness (H) with a relatively low elastic modulus (E) (to provide increased toughness). These coatings thus minimise the E/H ratio - which is known to be a parameter which is closely related to wear resistance. Other developments involve so-called 'hybrid' or 'duplex' combinations of processes to fulfil specific tribological needs. We are now in sight of achieving functionally-graded coating structures which combine tough and stress-equalised bulk properties, together with the extreme hardness, thermal and chemical properties of the exterior. The paper discusses the developments which have been necessary to achieve this - such as optimisation of compound compositions in the case of nanostructured composites based on nitride, carbide and boride phases. Also in the case of hard oxide ceramics, mention is made of growth modelling studies and plasma process developments to achieve the desired phases.

9:00am **TF+VM-MoM3 Ion-Assisted Filtered Cathodic Arc Deposition (IFCAD) Technology for Production of Superhard Thin-Film Coatings***, **M.L. Fulton**,* Ion Arc Corporation

A new Ion-Assisted Filtered Cathodic Arc Deposition (IFCAD) system has been developed for low temperature production of superhard thin-film coatings. Only ions within a well defined energy range arrive at the substrate surface depositing thin-films with excellent mechanical and optical properties.@footnote 1@ The new IFCAD system consists of a cylindrical rotary deposition chamber with two (or four) Filtered Cathodic Arc (FCA) sources, each associated with an end-Hall Ion-Assisted-Deposition (IAD) ion gun.@footnote 2@ By coupling IAD with FCA the development of cost effective deposition processes for applying superhard advanced thin-film materials such as: Amorphous Diamond-Like-Carbon (A-DLC); Aluminum Oxide (Al2O3); Aluminum Nitride (AlN); Carbon Nitride (C3N3); Titanium Nitrite (TiN); Titanium Nitride Carbide (TiCN); Titanium Oxide (TiO2: Rutile); and others in multi-layer thin-film structures suitable for tribological and electro-optical applications is now feasible. The IFCAD film properties are superior to other processes at elevated deposition temperatures, for example: the A-DLC thin-films have a micro-hardness in excess of 50 GPa (Diamond = 100 GPa); and the amorphous Al2O3 films have a hardness in excess of 20 GPa (bulk sapphire is 35 GPa). This new IFCAD technology has been included in advanced commercial, military and space development programs, such as: EUV mirrors; plastic and glass lens coatings for optical systems; wear resistant coatings on various metal substrates; and ultra smooth, durable, surface coatings for injection molds. @FootnoteText@ @footnote 1@ P. J. Martin, R. P. Netterfield, A. Bendavid, and T. J. Kinder, "The deposition of thin films by filtered arc evaporation," Surface and Coatings Technology, 54/55 (1992) 136-142. @footnote 2@ M. L. Fulton, "Application of ion-assisted-deposition using a gridless end-Hall ion source for volume manufacturing of thin-film optical filters," in Optical Interference Coatings, Florin Abeles, Editor, Proc. SPIE 2253, (1994) 374-393.

9:20am **TF+VM-MoM4 High Rate Reactive DC Magnetron Sputtering of Al Oxide and W Oxide Thin Films; Large Area Coatings***, **M.K. Olsson**,* Fraunhofer Institute for Solar Energy Systems, Germany*; K. Macák,* Linköping University, Sweden

Recently we reported stable high-rate deposition of Al oxide with any composition, including stoichiometry, utilizing a conventional reactive DC magnetron sputter system in laboratory scale.@footnote 1,2@ Due to the proper system geometry, including large enough target-to-substrate distance, and/or sufficient process gas pressure, it was possible to keep the target in the metallic mode by taking advantage of the scattering of the sputtered Al atoms through the inert gas. Moreover, the relatively high working pressure caused an increase in the back-deposited Al atoms to the non-eroded areas of the target, thus keeping these areas conducting, thereby avoiding arcing, without requiring the use of any other devices. We have applied this concept to a sputtering system considered for large area thin film production. A construction for increasing the cathode-to-sample length was designed with our technical possibilities in mind. After installation the desired O/Al arrival ratio was obtained and it was possible to produce stoichiometric aluminum oxide with an order-of-magnitude higher deposition rate. Choice of a sufficient pressure was crucial for the long-term stability of the process.@footnote 3@ Once the target is in the metallic state one may increase the growth rate linearly by increasing the target current. However, the experiments and analysis of the deposition process based on MC simulation of sputtered particles transport extended by Rossnagel's model of gas heating@footnote 4@ confirmed that the efficiency of the gas scattering process is for heavy elements partially eliminated at high discharge currents. To deal with this, we applied our concept of proper choice of process conditions for sputtering to less reactive materials with relatively high atom mass. It was possible to improve the sputtering condition for making films of stoichiometric amorphous W oxide at relatively high target current.@footnote 5@ @FootnoteText@ @footnote 1@M. Kharrazi Olsson, K. Macák, U. Helmersson, and B. Hjörvarsson, J. Vac. Sci. Technol. 16, 639 (1998). @footnote 2@K. Macák, T. Nyberg, P. Macák, M. Kharrazi Olsson, U. Helmersson, and S. Berg, J. Vac. Sci. Technol. 16, 1 (1998). @footnote 3@M. Kharrazi Olsson, K. Macák, W. Graf, Submitted. @footnote 4@S.M. Rossnagel, J. Vac. Sci. Technol. 6, 19 (1988). @footnote 5@M. Kharrazi Olsson, K. Macák, Submitted.

9:40am **TF+VM-MoM5 Elastic and Plastic Behaviors of Al/TiN Multilayered Thin Films Evaluated by Nanoindentation***, **E. Kusano**, Y. Sawahira, N. Kikuchi, H. Nanto, A. Kinbara,* Kanazawa Institute of Technology, Japan

Elastic and plastic behaviors of multilayer films of Al (Young's modulus:70GPa) and TiN(Young's modulus:350-400GPa) have been investigated for various layer numbers with different total Al thicknesses in order to reveal the role of hard TiN and soft Al layers on nanomechanical properties in multilayered films. Both Al and TiN layers were deposited by dc magnetron sputtering. Aluminosilicate glass was used as substrate. The number of layers prepared was 4, 20, and 40 for the total Al thickness of 100-500nm. The total thickness of TiN layers was kept at 500nm, including the top layer of 250nm. The microhardness and Young's modulus of the films were evaluated by nanoindentation. The energies consumed for elastic and plastic deformations were calculated from the load-displacement curve obtained by the indentation. The microhardness decreased with increasing the total Al thickness. The hardness enhancement by the multilayer structure was observed for 20- and 40-layer films with Al layer thicknesses of 10 or 5nm (the total thickness of 100nm) and TiN layer thicknesses of 26 and 13nm. The energy dissipated during the indentation also increased with the total Al thickness. The dissipated energy for films with 40 layers of Al/TiN was smaller than that for the films with 4 or 20 layers of Al/TiN for all Al thicknesses. In contrary, the elastic energy was independent both of the total Al thickness and of layer numbers. As a result, the ratio of dissipated energy to the loaded energy during the load/unload of the indentation yielded a minimum at an Al thickness of 100nm for 40-layer films. The ratio at the minimum was about 20% smaller than that of the monolithic TiN film. This means that the 40-layer film with a total Al thickness of 100nm is more elastic than the monolithic TiN. It is concluded that the enhancement in the film microhardness for multilayered films with thin Al layers is related to the decrease in the dissipated energy.

10:00am **TF+VM-MoM6 Gas-phase Chemistry in Up-scaled Plasma Enhanced MOCVD of TiN and Ti(C,N) on Plasma Treated Tool Steel***, **J.P.A.M Driessen**, A.D. Kuypers,* TNO Institute of Applied Physics, The Netherlands*; J. Schoonman,* Delft University of Technology, The Netherlands

In this paper, the deposition of TiN and Ti(C,N) in a relatively large scale reactor vessel is discussed. Tetrakis(dimethylamine)titanium (TDMAT) and tetrakis(diethylamine) titanium (TDEAT) were used for the purpose of depositing TiN and Ti(C,N) at low temperatures. In large scale systems, homogeneous reactions dominate the deposition process resulting in non-uniform and non-adherent coatings. However, in this study, favourable gas-phase conditions for deposition of Ti(C,N) from in a pulsed DC-plasma have been determined, making use of mass and optical spectroscopy. Decomposition of TDMAT in a pure hydrogen plasma results in the favourable cleavage of dimethylamine from TDMAT but prevents the formation of Ti(C,N) due to the lack of nitrogen and carbon. Addition of N@sub 2@ to the hydrogen plasma results in the formation of NH@sub x@ (1@<=@x@<=@4), opening transamination pathways. Results suggest that transamination plays an important role in the gas-phase of our system. Furthermore, these results were compared with those obtained from using ammonia. However, the depletion of TDMAT by interaction with nitrogen in a H@sub 2@(85%) - N@sub 2@(15%) plasma proceeds in a mechanistic step with a rate constant of k = 4.7 x 10@super -14@ cm@super 3@ mol@super -1@sec@super -1@. Nevertheless, seemingly high quality Ti(C,N) coatings were deposited on blank WN1.2370 tool steel and WN 1.2379 treated in a N@sub 2@/H@sub 2@ plasma. XRD analysis of the plasma treated substrate indicates the presence of CrN, among other species in the top surface layer. These multi-layer coatings, deposited at temperatures between 473 K and 698 K, increased in surface roughness, however, showed good adherence and optimum hardness. Hardness values varied from 1600 Hv to 2000 Hv.

10:20am **TF+VM-MoM7 Effect of Ion-to-neutral Ratio and Ion Energy on Structure and Properties of Boron Nitride Thin Films***, **M.U. Guruz**, Y.W. Chung, V.P. Dravid,* Northwestern University

Boron nitride thin films were deposited by dc reactive magnetron sputtering using a B@sub 4@C target in a single cathode chamber. The films were grown on Si (001) wafers, held at ambient temperature. The energy of the ions arriving at the substrate surface was determined by the applied bias. Additionally, an external coil assembly was placed outside the chamber, allowing modification of the magnetic field around the substrate. By varying the field strength, the ion flux on the substrate was enhanced. Thus, the ion-to-neutral ratio and the ion energy were independently controlled during deposition. The effects of these two parameters on the resulting film microstructure were investigated by transmission electron microscopy (TEM), atomic force microscopy (AFM), Fourier transform infrared spectroscopy (FTIR) and nanoindentation. These results and the effects on the formation of cubic boron nitride will be presented.

10:40am **TF+VM-MoM8 Mechanical Properties of Cubic Boron Nitride Thin Films Synthesized by ECR PECVD: Influence of Deposition Conditions***, **M.P. Delplancke-Ogletree**, M. Ye,* Université Libre de Bruxelles, Belgium

Cubic boron nitride containing thin films were deposited on (100) Si and steel substrates by electron cyclotron resonance plasma enhanced chemical vapor deposition. The films contain at least 55% of the cubic phase and are 0.5 µm thick. We investigated the dependence of hardness, stress, adherence, friction coefficient and wear resistance as a function of deposition parameters. The studied parameters are substrate bias, gas mixture composition, substrate temperature and processing pressure. These parameters are also correlated to the plasma characteristics measured by Langmuir probe, and mass spectrometer. Nanoindentation, scratch test, cantilever deflection, and ball-on-disk methods were used to evaluate quantitatively the mechanical properties. Films containing 55% of cubic phase are adherent to the two types of substrates, and have stress below 5 GPa.

11:00am **TF+VM-MoM9 Plasma Assisted Physical Vapour Deposition of BN by DC Pulsed Sputtering of a B@sub 4@C Target***, **L.A. Gea**, G. Ceccone, F. Rossi,* European Commission Joint Research Centre, Italy

Boron nitride coatings were deposited on Si (100) polished crystals by DC pulsed magnetron sputtering of a B4C target with auxiliary microwave Distributed Electron Cyclotron Resonance (DECR) plasma.The substrates were biased by an independent R.F. source. Characterization of the plasma was undertaken as a function of the total pressure, the nitrogen gas content and the microwave power. The presence of the various species was identified with Optical Emission Spectroscopy.Mass Spectrometry was used to determine the ion energy distribution while the plasma potential and the plasma densities were measured with a single Langmuir probe.The coatings have been characterized by Scanning Electron Microscopy (SEM), Auger Electron Spectroscopy (AES), and Fourier Transformed Infrared Spectrometry (FTIR)

11:20am **TF+VM-MoM10 Field Emission from Flat, Diamond-like Carbon Films Characterized by Scanning Force Microscopy***, T. Inoue,* Electrotechnical Laboratory, Japan*; **D.F. Ogletree**, M. Salmeron,* Lawrence Berkeley National Laboratory

Thin films of various diamond-like and carbon based materials on flat cathodes show significant field emission at relatively low voltages, but the exact emission mechanisms are not well understood. Non contact scanning force microscopy with a conductive tip in vacuum, used in the scanning polarization force mode (SPFM) , can detect and characterize emission sites with 100 nm lateral resolution. The SFM tip serves as an anode. It can be scanned over the surface to simultaneously measure local emission currents and local work functions. The tip-sample spacing and the tip bias can be varied to investigate mechanisms. Contact SFM images of emitting regions show local topography, reveal the presence of asperities, and characterize sample conductivity. For one type of CVD cathode material on an Si substrate, the emission sites were found to be (a) ~ 1 micron in diameter (b) not associated with asperities at the cathode-vacuum interface (c) not associated with low work function regions, and (d) semiconducting with a large band-gap. I-Z data indicate that emission takes place within the film, or at the film-substrate interface, rather that at the film-vacuum interface. Single-site emission currents were strongly modulated on a ~ 1 ms time scale, possibly due to charge trapping. Surface potential shifts were correlated with the emission current fluctuations.

11:40am **TF+VM-MoM11 Effect of Nondiamond Carbon on the Electron Transport Path of Field-emitted Electrons from Undoped Polycrystalline Diamond Films***, **J.Y. Shim**,* Yonsei University, Republic of Korea*; K.M. Song,* Konkuk University, Republic of Korea*; H.K. Baik,* Yonsei University, Republic of Korea, KOREA

Diamond has attracted considerable interest recently as a promising field emitter material because of its important properties such as NEA, high thermal conductivity, and low field electron emission. Among the properties, understanding the origin of low field emission is a key factor for the application of diamond to a field emitter. Many investigations have been extensively drawn to clarify the origin of low field emission behavior of diamond. Suggested models explaining the low field emission behaviors up to now are the discontinuous graphitic inclusions in CVD diamond matrix, the defect induced subbands, and the surface emission from metal-diamond-vacuum interface. Besides, there have been several reports on the importance of the electron transport through the substrate/diamond interface. However, the origin of the low field emission behavior is still unclear, and those may be different between diamond crystal and CVD diamond films. It is expected that the field emission mechanism of undoped polycrystalline diamond films can be changed by the structural properties. The present study is mainly focused on the electron transport through the substrate-diamond interface and the diamond layer, and the resulting field emission mechanism of undoped polycrystalline diamond films with different structural properties. In order to examine field emission properties of undoped polycrystalline diamond films, we have prepared the diamond films with different structural properties and/or different substrate-diamond interfaces. It was observed that transport paths of field-emitted electrons could be clearly identified from the spatial distributions of emission sites and the nondiamond carbon content obtained from the diamond films, and the characteristics of the substrate-diamond could modify the field emission properties. From the present study, a possible field emission mechanism for the undoped polycrystalline diamond films is suggested.

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Room 615 - Session TF-MoM
Fundamentals of PECVD

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

8:20am **TF-MoM1 Investigation of the Plasma Properties and Fluxes in a Hydrogenated Amorphous Carbon Deposition Process***, B.K. Kim,* ***T.A. Grotjohn,*** Michigan State University

The deposition process and conditions used for hydrogenated amorphous carbon (a-C:H) film deposition from acetylene, acetylene-helium, and acetylene-argon gas mixtures in a microwave ECR plasma reactor are studied. This paper quantifies the plasma discharge fluxes to the substrate based on experimental measurements and plasma discharge modeling. The film properties are also correlated to the plasma discharge conditions. The films are deposited on glass and silicon substrates which are placed on an rf biased (13.6 MHz) substrate holder located just at the exit of a multipolar, permanent magnet ECR plasma source operating at 2.45 GHz. The deposition parameters varied during this investigation included rf induced dc substrate bias voltage (-50 to -300 V), pressure (0.1-1.0 mTorr) and argon/acetylene (or helium/acetylene) gas flow ratio. The properties of the plasma discharge measured include electron temperature, ion saturation current, and residual gas composition. The films deposited with different gas mixtures, pressures and rf biases have substantially different properties including deposition rate, mass density, optical absorption coefficient, optical bandgap and hydrogen content. The use of lower pressures to obtain an increased ion-flux/neutral-flux ratio to the substrate was found to be critical for obtaining dense, low hydrogen content films from acetylene. The addition of argon and helium were found to substantially change the plasma discharge deposition conditions, as well as, influence the deposited film properties.

8:40am **TF-MoM2 Time-resolved Study of C@sub x@N@sub y@ Growth by Means of Fourier Transform Infrared Reflection Spectroscopy***,* ***A. de Graaf****, B. Schreur, M.C.M. van de Sanden, D.C. Schram,* Eindhoven University of Technology, The Netherlands

Fourier transform infrared (FTIR) reflection spectroscopy is used to study the composition of carbon nitride (C@sub x@N@sub y@) films in situ during the early stages of growth and during etching. The C@sub x@N@sub y@ films are deposited from a thermal Ar/N@sub 2@ plasma expanding through a graphite nozzle. The graphite is chemically etched leading to strong CN emission both at the nozzle exit and at the substrate level 65 cm downstream. The observation of C@sub 2@N@sub 2@ in the mass spectrometer gives further support to the idea that CN radicals are formed during deposition. In order to measure small reflection changes on a (sub)monolayer level and on a short enough time scale, a special substrate has been developed which enhances the IR absorption considerably at a specific wavelength. With this substrate the evolution of the different bonds (sp@super 1@, sp@super 2@ and sp@super 3@ C-N) in the film can be followed. The results show a relative increased absorption of the sp@super 1@ C-N bond during initial growth as compared to the absorption in the bulk material. This strongly suggests that CN radicals are indeed involved in the deposition. After film growth the absorption of sp@super 1@ C-N bonds decreases while the absorption of sp@super 2@ C-N bonds increases. Etching of the C@sub x@N@sub y@ films by an expanding Ar/N@sub 2@ or Ar/O@sub 2@ plasma also shows a different response in the absorption signal of sp@super 1@ C-N as compared to sp@super 2@ C-N. The optical constants of the material and growth rate are derived from an optical model and are correlated to in situ ellipsometry measurements performed simultaneously. Based on these findings a tentative growth model is presented. In a next step this model will be extended to describe deposition at different substrate temperatures and bias voltages.

9:00am **TF-MoM3 Surface Reactions of CH@sub x@ and SiH@sub x@ Radicals during Plasma Deposition of a-C:H and a-Si:H Films***,* ***A. von Keudell,*** Max-Planck-Institut für Plasmaphysik, Germany **INVITED**

The surface reactions of CH@sub x@ and SiH@sub x@ radicals as the dominant growth precursor during plasma deposition of amorphous hydrogenated carbon and silicon films are investigated by exposing a-C:H and a-Si:H film surfaces to low temperature plasma discharges or to quantified radical beams. The surface reactions are monitored in real time by using in-situ ellipsometry and in-situ infrared spectroscopy. The measurement of the surface reaction probability of various hydrocarbon radicals indicates that the reactivity of larger C@sub x>1@H@sub y@ radicals at the a-C:H surface is much higher than that of CH@sub y@ radicals. This has several consequences for the understanding of a-C:H film growth, which will be described in detail. The deposition of a-Si:H from silane discharges is assumed to be similar to the growth of a-C:H films since in both cases the dominant growth precursor is CH@sub 3@ or SiH@sub 3@, respectively. However, the dominant interaction mechanism of silyl radicals with a-Si:H surfaces, as identified by isotope labeling experiments, is very different to that of CH@sub 3@ radicals on a-C:H surfaces. Whereas methyl radicals can only adsorb at open bonds at the a-C:H film surface, silyl radicals are able to insert into strained bonds at the a-Si:H surface. A comparison of microscopic growth processes during a-C:H growth and a-Si:H growth will summarize this presentation.

9:40am **TF-MoM5 Quantitative Characterization of a Particle Beam Source for Atomic Hydrogen and Hydrocarbon Radicals for Thin Film Growth Studies***,* ***Th. Schwarz-Selinger****, A. von Keudell, W. Jacob,* Max-Planck-Institut für Plasmaphysik, Germany

Hydrocarbon radicals are the dominant neutral growth precursors for the deposition of amorphous hydrogenated carbon films (a-C:H). For the investigation of the growth mechanisms a particle beam source was developed, which is able to produce thermal beams of neutral hydrocarbon radicals. The radicals are produced in a resistively heated tungsten capillary by thermal dissociation at the hot walls of the capillary. The maximum temperature of the capillary, achievable is around 2600 K, which is sufficient to also produce atomic hydrogen from H@sub 2@ with a high yield. A rotatable (@+-@ 20°) quadrupole mass spectrometer in line of sight to the capillary exit was employed to study the emanating particle beam. This setup allows to identify the emitted species and their angular distribution and permits to quantify the emitted fluxes. For hydrogen the degree of dissociation and the total flux of atomic hydrogen as a function of temperature and gas flow is presented. With the same source methyl radicals are produced. Results are presented for the total amount of methyl radicals using different hydrocarbon source gases. First results of surface reactions of these radicals, investigated by monitoring the interaction of the particle beam with a-C:H film surfaces in real time by in-situ ellipsometry and in-situ infrared spectroscopy, complete this presentation.

10:00am **TF-MoM6 High Rate a-Si:H Growth Studied by in situ Ellipsometry***,* ***A.H.M. Smets****, B.A. Korevaar, W.M.M. Kessels, M.C.M. van de Sanden, D.C. Schram,* Eindhoven University of Technology, The Netherlands

In this contribution the results of in-situ HeNe rotating compensator ellipsometry measurements performed on hydrogenated amorphous silicon (a-Si:H) growth using an expanding thermal plasma are presented. This remote thermal plasma technique is developed as a promising tool for high deposition rate (10 nm/s) of a-Si:H on a roll to roll production line of low cost thin film solar cells on a flexible foil. The measurements can be simulated using an optical growth model consisting of a substrate layer, SiO@sub 2@ layer, intermediate layer, a-Si:H bulk layer and a top layer, corresponding to the surface roughness. Using this model the roughness evolution during deposition can be monitored. At deposition conditions at which "device quality" a-Si:H is grown the surface roughness is the smallest, indicating that roughness and material quality are related. The correlation between incorporation of SiH@sub 2@ complexes and the surface structure will be discussed. From the roughness evolution in time at various substrate temperatures the length scales which dominate the high rate a-Si:H growth can be deduced. The activation energy of the diffusion processes is also determined and its significance for the Matsuda-Perrin-Gallagher growth model will be discussed.

10:20am **TF-MoM7 Ab-initio Study of H Abstraction from Amorphous Silicon Surface By Hydrogen and silyl(SiH@sub 3@) Radicals: Implications for Stability of 3-center Bond Formation***,* ***A. Gupta****, H. Yang, G.N. Parsons,* North Carolina State University

Plasma deposition of amorphous and micro-crystalline silicon from silane/hydrogen gas mixtures is widely utilized in the manufacture of solar cells and in thin film transistors (TFT) required in the active matrix liquid crystal displays (AMLCD). A fundamental understanding of the surface reactions that may result in the removal of bonded H will be useful to further optimize the deposition process. The surface H may be abstracted by H or SiH@sub 3@ radicals to form H@sub 2@ or SiH@sub 4@ respectively leaving behind a dangling bond which provides an active site for chemisorption of SiH@sub n@ radicals. It has been proposed that the first step in a-Si deposition is the formation of a stable 3-center (Si-H-Si) bond by the SiH@sub 3@ radicals and the surface hydrogen groups but the energetics of this elementary step are unknown. We have used configuration interaction (CI) and density functional (DFT-BLYP) calculations to compare the abstraction of surface hydrogen by H as well as SiH@sub 3@ radicals. Our results indicate that the H radicals are more likely to abstract the surface H compared to the SiH@sub 3@ radicals. The activation energy for the former reaction was determined to be ~5.5 kcal/mol and the heat of reaction was ~-11 kcal/mol while the latter reaction had an activation energy ~9.4 kcal/mol and an energy change ~-6 kcal/mol. Thus we can conclude that the H radicals are more likely to abstract the hydrogen from the Si(111) surface as compared to SiH@sub 3@ radicals. The potential energy surface for the reaction of SiH@sub 3@ radicals with the surface H generated using the DFT method does not indicate the presence of a stable 3-center bond within the accuracy of the method. The activation energy using this method was ~6 kcal/mol and the reaction energy was ~-7 kcal/mol. These results indicate that long-standing models for surface and bulk bond structure development need to be re-examined and support the possibility of other reaction schemes viz. SiH@sub 3@ insertion into Si-Si bonds on the surface.

10:40am **TF-MoM8 Impact of Helium Dilution on Low-Temperature Silicon Depositions Using Electron Cyclotron Resonance and RF Plasma Sources***,* ***S.H. Bae****, Y.C. Lee, R.T. McGrath,* Pennsylvania State University

Low temperature silicon films have been prepared at 110° C using electron cyclotron resonance (ECR) plasma, ECR plasma plus RF substrate bias, and RF plasma only. As dilution media, both pure hydrogen and hydrogen mixed helium gases have been employed for these low-temperature depositions. In order to relate the plasmas to the properties of these low temperature Si films, in-situ optical emission spectrum (250 ~ 800 nm) for each plasma condition has been examined. Regardless of the presence of RF substrate bias during ECR plasma depositions, intensity of optical emission of ECR plasma much higher than that conventional RF plasma. In the ECR plasmas, the emission intensities of H radicals much stronger than those in RF plasma mode by two order of magnitude. In both H @sub 2@ and H@sub 2@ +He diluted RF plasmas, H @gamma@ (434 nm) and H @beta@ (486 nm) emissions are not noticeable for 0.6 second integration of optical spectrum while H @alpha@ (656 nm) line is observable in the RF plasma. Addition of He gas in ECR plasma results in strong He radical emission lines (389 nm and 502 nm); i.e., this indicates highly excited hydrogen plasma can be produced by the metastably excited He radicals. X-ray diffraction (XRD) analysis shows that low-temperature pure RF mode Si films do not have any crystallinity regardless of addition of He gas while the Si films prepared with ECR plasmas have high crystallinity. However, these high-crystallnity low-temperature ECR films are very porous and columnar. In terms of micro-etching effect due to hydrogen radicals in high-density plasmas, H @sub 2@+He dilution is more efficient than the case of H@sub 2@ dilution.

11:00am **TF-MoM9 Hydrogenated Amorphous Silicon Surface Growth Mechanism Characterized by Fourier Analysis of the Surface Topography***,* ***K.R. Bray****, A. Gupta, L. Smith, G.N. Parsons,* North Carolina State University

Hydrogenated amorphous silicon (a-Si:H) is widely used for the manufacture of solar cells and for thin film transistors (TFT) in active matrix liquid crystal displays (AMLCD). There have been many studies of the gas-phase reactions occurring in the plasma, but less is known of what takes place on the growing silicon surface. An increased understanding of its growth mechanism is desirable to optimize the quality of the a-Si:H films. Atomic force microscopy (AFM) was used to image the surface topography of PECVD deposited a-Si:H. Surface topography was compared for samples deposited over a wide range of temperatures (25° C - 350° C) and film thicknesses (20 - 2000 Å). The rms surface roughness has been used to characterize surface growth. During the initial 30 seconds of nucleation using 100 sccm of 2% SiH@sub 4@/He, the rms is between 1 - 4 nm. As the deposition continues from 1 to 5 minutes, the rms increases to between 13 and 28 nm. After film coalescence, the rms roughness reduces to between 1 and 4 nm. A Fourier analysis of the surface topography produces an index (i), which has been correlated with different surface growth mechanisms. The Fourier indices for these samples range from i = 3.8 to 4.8, and increase with temperature. These results indicate that surface diffusion (i = 4) is the primary smoothing mechanism during growth. But the deviation from 4 suggests that the actual mechanism is more complex than simple surface diffusion. A shift in i suggests that there is a change in the growth mechanism as the film coalesces. We will discuss correlations between the Fourier index and film quality as deduced from structure and electrical characterizations.

11:20am **TF-MoM10 Deposition of Silicon Oxide Films using a Remote Thermal Plasma***, M.C.M. van de Sanden,* ***M.F.A.M. van Hest****, D.C. Schram,* Eindhoven University of Technology, The Netherlands

A cascaded arc (p=0.1 â€“ 0.2 bar) has been used to generate a remote thermal argon plasma, which expands into a vacuum vessel (p=0.1 mbar). In this expanding thermal argon plasma oxygen is injected at the arc nozzle. Downstream HMDSO (hexamethyldisiloxane) is injected as a precursor. The cascaded arc as a plasma source has some big advantages in comparison to the more conventional techniques (i.e. CVD). The first advantage is that the deposition rate obtained is much higher with the use of the cascade arc (>100 nm/s) than with the use of conventional techniques (couple of nm/s). The second advantage is that the deposition rate does decrease with increasing substrate temperature. Therefore it is not necessary to heat the substrate to very high temperatures (>500°C) before the film can be deposited. The deposited films have been analysed using in situ ellipsometry, elastic recoil detection (ERD), and in situ Fourier transform infrared reflection absorption spectroscopy. Ellipsometry shows that the deposited films have good optical properties. FTIR absorption spectrosopy measurements as well as ERD measurements show that the deposited films contain carbon. To get a better understanding of the film growth, in situ FTIR reflection absorption spectroscopy measurements are done. The effect of post deposition plasma exposure is discussed. The gas phase of the depositing plasma has been analysed by means of mass spectrometry and gas phase FTIR absorption spectroscopy. These measurements show that in the gas phase new stable species (i.e. C@sub 2@H@sub 2@) are created.

11:40am **TF-MoM11 Dielectric Properties of Silicon Nitride Deposited by High Density Plasma Enhanced Chemical Vapor Deposition@footnote 1@***,* ***J.B.O. Caughman****, D.B. Beach, G.E. Jellison, W.L. Gardner,* Oak Ridge National Laboratory

The dielectric properties of silicon nitride films have been investigated. The films were deposited on silicon substrates at temperatures <400 degrees C by using a high density inductively coupled plasma source. The plasma source is operated at 13.56 MHz using a flat spiral coil. A nitrogen plasma is formed in the ionization region of the source and 100% silane is injected downstream. Properties of the films are determined by using 2-modulator generalized ellipsometry and FTIR. Growth rates vary from 20-45 nm/min, depending on the processing parameters. For nitrogen/silane gas flow ratios of 0.25 to 10.0, the refractive index of the films (at 350 nm) vary little and are around 1.82. The band gap ranges from 4.5 to 6.2 eV. The addition of hydrogen in the ionization region results in an increase in the refractive index and a reduction in the band gap. For nitrogen/silane ratios of 0.25 to 2.0, the refractive index varies from 2.18 to 1.95 and the band gap varies from 3.1 to 4.4 eV. In addition, the hydrogen content in the film actually decreases with the addition of the hydrogen in the ionization region. A mass spectrometer imbedded in the substrate is used to correlate film properties with processing parameters. It is believed that the addition of the hydrogen increases the reactivity of silane in the gas phase, and that the flux of atomic hydrogen at the surface helps to abstract hydrogen from the growing film. @FootnoteText@ @footnote 1@ORNL is managed by Lockheed Martin Energy Research Corp. for the U.S. Department of Energy under contract no. DE-AC05-96OR22464.

Applied Surface Science Division
Room 610 - Session AS1-MoA

Molecular Mass Spectrometry including Interpretation

Moderator: S.J. Pachuta, 3M

2:40pm **AS1-MoA3 Interpretation of Static SIMS Spectra***, **D. Briggs,*** Siacon Consultants Ltd., U.K. **INVITED**

Static SIMS has rapidly developed into a powerful tool for the molecular characterisation of surfaces, with modern time-of-flight (ToF) instruments capable of providing both high mass resolution (m/@DELTA@m >7000)and high spatial resolution (~ 0.1 micron). Although most of the emphasis to date has been in the application to organic/polymeric systems the technique has equal potential for the surface characterisation of inorganic materials. However, the information content of ToFSIMS spectra is enormous and the interpretation of 'unknown' spectra consequently poses a serious challenge. There is a widespread feeling that the full exploitation of the technique is limited by interpretation problems, particularly with the pressure to deskill/automate all analytical operations. Compared with other forms of mass spectrometry and especially EI-MS, SIMS presents extra problems for spectral interpretation: the physical basis of the ion formation process is very poorly understood, the spectra are influenced by the primary ion used and by the matrix from which the ions originate and there are no established 'rules' for fragmentation. The development of searchable databases of standard spectra has been a key feature of other molecular spectroscopies and this approach clearly represents a way forward for SIMS. Aspects of the development of the only stand-alone database@footnote 1@ will be discussed in the light of these issues. @FootnoteText@ @Footnote 1@The Static SIMS Library, SurfaceSpectra Ltd, Manchester, UK

3:20pm **AS1-MoA5 Characterization of Polymer Additives by Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS)***, **R. Kersting,*** TASCON GmbH, Germany*; R. Verlaek,* DSM Research, The Netherlands*; B. Hagenhoff,* TASCON GmbH, Germany*; A.P. Pijpers,* DSM Research, The Netherlands*; B.C. Schwede,* ION-TOF GmbH, Germany

Polymers used for industrial purposes generally contain various additives to improve the product performance. Substance classes include anti-oxidants, plasticizers and flame retardants. Typical concentrations are in the order of some 100 to 1000 ppm. Although much is known about the bulk composition of the additive containing polymer not many information on the surface composition of real industry polymers is available. Generally, Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS) is an ideally suited analytical technique to characterize the surface composition because it offers detailed molecular information with high sensitivity. On the other hand the surface concentration in real world systems can be very small, even below the detection limit of normal TOF-SIMS analysis. Therefore most TOF-SIMS studies of polymer additives have concentrated on pure materials or highly concentrated model systems. Recently, we have started a systematic study on the secondary ion emission behaviour of polymer additives using model systems containing the additives in their normally applied concentrations and embedding them into their normal host polymer. The study aims at the automated identification of additives in real world samples from their TOF-SIMS spectra. Special emphasis is therefore laid on the emission pattern for use in a spectra library and the determination of detection limits. Different primary ion bombardment conditions (monoatomic primary ions: Ar@super +@, Ga@super +@; polyatomic primary ions: SF@sub 5@ @super +@) were used to study the influence of primary ion mass and polyatomicity on the secondary ion emission. We will present our first results obtained on antioxidants. Whereas most substances can be analyzed to satisfaction using primary ions like Ar@super +@ or Ga@super +@, it turned out that in some cases polyatomic primary ions (SF@sub 5@ @super +@) had to be used in order to reach acceptable detection limits.

3:40pm **AS1-MoA6 Secondary Ion Emission from LB-Layers Under Molecular Primary Ion Bombardment***, **D. Stapel,** M. Thiemann,* Universität Münster, Germany*; B. Hagenhoff,* TASCON GmbH, Germany*; A. Benninghoven,* Universität Münster, Germany

Secondary ion yields Y(X@sub i@@super q@) increase considerably when changing from atomic to molecular primary ions, whereas 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. The secondary ion emission of well defined model LB systems were investigated for a more detailed understanding of the complex sputtering and ion formation processes especially under different molecular primary ion bombardment. We investigated three series of LB layers (n=1, 3, 5, 7 ; n : number of monolayers) under 1 - 10 keV O@super +@, 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. Our experimental results demonstrate a more pronounced yield and efficiency enhancement for multilayers (n>1). The increase in 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 (SF@sub 5@@super +@/C@sub 7@H@sub 7@@super +@ e.g.) on this enhancement under static SIMS conditions. We compared the secondary ion and secondary neutral emission depths under atomic and molecular primary ion bombardment, and determined the influence of primary ion energy on secondary ion emission.

4:00pm **AS1-MoA7 Enriched Spectral-information from TOF-SIMS Spectra of Self Assembled Monolayers: More Than Just Molecular Ions***, D.J. Graham, **B.D. Ratner,*** University of Washington

Engineered biomaterials that accurately trigger complex biological processes such as healing require complex surface modifications. This increase in complexity must be met by equally capable surface analysis tools such as TOF-SIMS. To extract information from complex organic surfaces, one should consider the spectrum as a whole, instead of selecting only a few key peaks. This study demonstrates that the information content of a TOF-SIMS spectrum does not reside solely in the molecular and cluster ions, but that each region of the spectrum contains enough information to clearly distinguish the samples. For this study dodecanethiol self-assembled monolayers (SAMs) were prepared from 0.01mMol solutions in ethanol for different times (2sec,1min,5min,15 min,30 min,1hr,24hr,6d). Principal component analysis (PCA) models from the TOF-SIMS negative and positive spectra were constructed using the entire data set and from partial data sets from mass ranges m/z=0-100,100-200,200-300,400-500,500-1000. Scores plots from the PCA models show that data from each set were able to distinguish the samples. Regions containing the molecular ions showed enhanced ability to distinguish the samples. In the overall model it was seen that there is a relative increase in the intensity of low mass hydrocarbon fragments (C to C3) with increasing time. Similar trends were seen in the positive spectra where a relative increase of C to C4 hydrocarbon fragments was seen with increasing time. This increase was accompanied by a decrease in the intensity of C5 and above hydrocarbon fragments. 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. As there is also an enhancement of the emission of the thiol head group ion, it is believed that these short fragments arise by the clipping of the tops of the assembled layer by the primary ion or energetic secondary ions.

4:20pm **AS1-MoA8 Static SIMS with Polyatomic Primary Ions***, **A. Benninghoven,** D. Stapel, O. Brox, B. Burkhardt, H.F. Arlinghaus, C. Crone, M. Thiemann,* Universität Münster, Germany

Polyatomic primary ion bombardment results in an increase in secondary ion yields Y and damage cross sections @sigma@ in such a way that the ion formation efficiency E = Y/@sigma@ increases. Investigated samples include metal and semiconductor surfaces (Ag, Si, GaAs) in different oxidation states, bulk and spin coated polymers with additives (PET, PC, PI, PP, PTFE, PMMA, PEG), SA- and LB - mono and - multilayers (thioles, arachidic acid on Au, PMA on Ag), hydrocarbon contamination layers on Si and GaAs, monolayers of biomolecules on Ag and other substrates, and biopolymers, technical polymers and pharmaceuticals isolated in an organic matrix. They have been bombarded by a variety of primary ions in the keV range O, Ne, Ar, Xe, O@sub 2@, CO@sub 2@, SF@sub 5@, C@sub 7@H@sub 7@, C@sub 10@H@sub 8@, C@sub 6@F@sub 6@ and C@sub 10@F@sub 8@. For atomic primary ions we found an increase in secondary ion yields with increasing mass of the primary ion, but only relatively small increases in efficiency. Compared with atomic ion bombardment, molecular primary ion bombardment always results in a yield and efficiency enhancements. No significant influence of the chemical composition of the primary ions on secondary ion yields has been observed, as long as static SIMS conditions were met. Yield and efficiency enhancements show saturation behaviour for primary ions composed of more than 6 (heavy) atoms. We found a strong dependence of the enhancement effects on the considered secondary ion species and a smaller averaged secondary ion emission depth for molecular primary ion bombardment. We will summarize our experimental results and will discuss them in the frame of a simple model. Whereas yield and damage cross section enhancements can be explained - at least partially - by an increase in sputter yields, the observed increase in ion formation efficiencies for molecular primary ions indicates a more efficient ionization process for polyatomic primary ion impact.

4:40pm **AS1-MoA9 Quantitative ToF-SIMS and XPS Studies of Surface Structures in Alkyl Side-Chain Polyetherurethanes***, **S.C. Porter**, D.G. Castner, B.D. Ratner,* University of Washington

Surface enrichment of polyether soft segment (SS) is typical in segmented polyetherurethanes (PEUs). The incorporation of surface active side-chains (SC) into the relatively polar hard segment (HS) block of the polymer significantly alters the surface structure. PEUs having various lengths and densities of alkyl SCs were synthesized. XPS analysis showed that PEUs with long SCs had high surface concentrations of hydrocarbon (HC) chains. Similarly, HS blocks were drawn toward, and concentrated just below, the HC rich surface. Positive ToF-SIMS spectra of these polymers contained fragments unique to both the HS and SS of the PEUs. Numerous HC fragments from the set, (@super+@C@sub x@H@sub 2x+1@ and @super +@C@sub x@H@sub 2x-1@; x @<=@ 7), could be indirectly associated with the length and/or density of alkyl SCs. Negative spectra contained fragments unique to individual SC species and HS fragments analogous to those found in the positive spectra. Ion ratios were used to determine the HS/SS (pos. spectra) and SC/HS (neg. spectra) surface concentration ratios. The HS/SS and SC/HS ratios increased with both side-chain length and density. Comparison of log(HS/SS) to actual concentration ratios obtained from XPS data, yielded linear correlations. The correlations improved as the sampling depth of the XPS experiments approached that of SIMS. The presence of isomeric HS fragment pairs in both positive and negative SIMS spectra provided an intrinsic reference for direct comparisons of the intensity of the positive HC fragments with a negative SC fragment. An analytical relation based on theoretical ion intensities was established for a series of PEUs having the same SC. Ion ratios from the positive spectra and a ratio from the negative spectra were shown to be directly proportional. The proportionality constant was solely a function of the ionization probabilities for the various ions utilized. HC fragments which did not contain contributions from either the HS or SS showed good correlations with the SC fragment intensity.

5:00pm **AS1-MoA10 Molecular Secondary Neutral Emission from Molecular Overlayers under SF@sub 5@@super +@-Bombardment***, **A. Schnieders**, M. Schröder, D. Stapel, H.F. Arlinghaus, A. Benninghoven,* Universität Münster, Germany

It is well known that TOF-SIMS and in favourable cases laser postionization of sputtered neutrals (Laser-SNMS) are powerful tools for the analysis of organic surface species. Many efforts have been made to enhance the sensitivity and the efficiency of these techniques. Especially the use of polyatomic primary ions for the analysis of molecular overlayers results in an enhanced secondary ion emission compared to the use of atomic primary ions. We have investigated the influence of polyatomic primary ions on the secondary neutral emission with the intention to improve our understanding of the processes of molecular sputtering and ion formation. We used a reflectron-type time-of-flight mass spectrometer equipped with an electron impact gas ion source for sputtering. As primary ion species we chose Ar@super +@, Xe@super +@, and SF@sub 5@@super +@. For postionization of sputtered neutral molecular species a subpicosecond excimer laser system operating at 248 nm was available. As model systems we used molecular layers of adenine and alanine prepared on liquid nitrogen cooled substrates (Si, Au, ...). They were produced by evaporation of the molecules from a Knudsen cell under UHV condition. During overlayer formation the flux of sputtered secondary neutrals and secondary ions was continuously monitored under static sputtering conditions. We determined the influence of the substrate and of the layer thickness on the secondary ion and neutral yields under bombardment with the different primary ions. We found that neutral as well as ion yields from a submonolayer coverage are higher than for a multilayer. The yield enhancement depends on the sputtering conditions. We also determined kinetic energy distributions and disappearance cross sections as a function of layer thickness. A detailed discussion with special emphasis on the sputter process - including results on the internal excitation of sputtered molecules - will be presented.

Applied Surface Science Division
Room 6A - Session AS2-MoA

Applied Surface Science for Microelectronics
Moderator: C. Magee, Evans East

2:00pm **AS2-MoA1 Determination by XPS of the Reactions Taking Place at the Semiconductor/'Heteropolyanion Solution' Interface***, A. Quennoy, A. Rothschild, A. Etcheberry,* CNRS - France*; **C. Debiemme-Chouvy**,* CNRS - France, FRANCE

When semiconductors (SC) are immersed in a solution containing oxydizing species they could undergo an oxidation/dissolution process. Therefore their surface chemical composition can evolve. The knowledge of the SC surface composition after the treatment allow sometimes to determine the reactions which had taken place at the SC/solution interface. In this communication, an example will be shown. The heteropolyanions (HPA) based on oxometallate compounds can undergo multiple one- or two-electron reduction of the metallic atoms. @footnote 1@ Thus depending on their oxidizing power they could oxidize SC. We studied the behavior in acidic solution of two HPA species with a Keggin structure H@sub 4@SiW@sub 12@O@sub 40@ (SiW@sub 12@) and H@sub 4@SiMo@sub 12@O@sub 40@ (SiMo@sub 12@) toward GaAs. The XPS analyses shown that after immersion in the HPA solution a deposit is formed on the GaAs surface. For immersion longer than one hour the substrate is no more detected. The deposit obtained in the presence of SiW@sub 12@ is composed of WO@sub 3@.@footnote 2@ Concerning SiMo@sub 12@, the HPA structure seems conserved in the deposit. Moreover the peak fitting of the Mo3p XPS spectrum indicates that some Mo atoms have remained at the oxidation state (VI) and that others have reached the oxidation state V. Otherwise, whatever the HPA studied As atoms are present in the deposit. They are at an oxidation state higher than that of As atoms inside the substrate. All these results indicate that in the presence of SiW@sub 12@ or SiMo@sub 12@ GaAs is oxidized while the HPA species are reduced. The conclusions obtained just on the basis of the XPS analyses were confirmed by electrochemical studies and profilometry. @FootnoteText@ @footnote 1@ M.T. Pope, Heteropoly and Isopoly Oxometalates, Springer, Heidelberg, 1983. @footnote 2@ A. Rothschild, C. Debiemme-Chouvy, A. Etcheberry, Applied Surface science 135 (1998) 65.

2:20pm **AS2-MoA2 Sputter Deposition and Annealing of Ta, TaSi and Ta@sub 4@B Composite Films and Their Application in Next Generation Lithography Masks***, **K. Racette**, C. Brooks,* IBM

Ta and Ta composites with other elements have been developed by several researchers as low stress absorbers for x-ray mask technology. These thin films are often produced in small quantities by sputter deposition from targets of pure Ta with chips of the minor elements placed on the target to create the composites. For membrane-mask manufacturing it is important that absorber films have uniform composition, thickness and low stress to assure that image size and pattern placement errors are minimal. Since sputter deposited films containing Ta have highly compressive stress, several methods have been used to reduce the final stress, including careful control of sputtering conditions, deposition of layered films with different stresses, and thermal annealing. Much data has been reported on the effects of thermal annealing of Ta films but less information is available on multiple element films such as TaSi and Ta@sub 4@B. Reports have generally been developmental in nature and not discussed behavior of these films under longer term, higher volume manufacturing conditions. During the last several years IBM has been engaged in development and fabrication of refractory x-ray membrane-masks using TaSi and Ta@sub 4@B as absorber materials. Films were sputter deposited from hot isostatically pressed powder targets of Ta, Si, and B using an S-gun cluster deposition system. This paper will report on the deposition and annealing of these films and their application to membrane-mask fabrication in a manufacturing environment. The effects of deposition parameters such as dc power, argon gas flow (pressure) and substrate on film stress, composition and density will be dicsussed. The results of air and nitrogen annealing on thick and thin films of TaSi and Ta@sub 4@B will be presented. Absorber film quality data and its impact on image size, pattern placement and defect density of some fabricated x-ray masks will be presented.

2:40pm **AS2-MoA3 XPS Sputter Depth Profiling at the Pd/Y Interface@footnote *@**, ***G. Neuert**, R.J. Smith,* Montana State University*; J.A. Schaefer,* Technische Universität Ilmenau, Germany

X-ray photoelectron spectroscopy (XPS) sputter depth profiling, Rutherford Backscattering Spectroscopy (RBS) and in situ resistivity measurements are used to study the Pd-Y interface. This interface is of interest because of recent work showing that Pd-capped Y films exhibit a reversible metal semiconductor transition as a function of H content in the film. The yttrium film was first evaporated on a glass substrate. A palladium layer was then evaporated on the top of the yttrium film. Both films are made by thermal evaporation using a tungsten basket with a boron-nitride crucible as heating shield. RBS is used to measure the thickness of the film and to calibrate the sputter rate for pure Pd and Y. Palladium 3d photoelectron peaks, measured by XPS, show a core level shift to higher binding energies with sputter depth. This chemical shift can be an indication of alloy formation at the Pd / Y interface. The resistance measurements are done in situ by a four probe measurement after van der Pauw. The resistance of the yttrium film is measured after finishing the yttrium evaporation. A palladium layer was then evaporated on the top of the yttrium and the resistance of the films was monitored during Pd evaporation. @FootnoteText@ @footnote *@Work supported by NSF DMR 97-10092 and NASA EPSCoR NCCW-0058. Permanent address of G. Neuert : Institut für Physik, Technische Universität Ilmenau, P.O. Box 100565, D-98684 Ilmenau, Germany.

3:00pm **AS2-MoA4 Thin Film Characterization through combined X-ray Photoelectron Spectroscopy (XPS) and X-ray Diffraction (XRD)**, ***D.J. Surman**, S. Bates,* Kratos Analytical Inc.*; C.J. Blomfield, A.J. Roberts,* Kratos Analytical Inc., UK*; J.E. Fulghum,* Kent State University

Traditionally there has been a range of methodologies applied to the analysis of thin films, centering on the use of XPS combined with sputter profiling. This approach provides both elemental and chemical information for each of the layers within the film. Following calibration with standard materials, a measure of the sputter rate can be obtained allowing allowing film thickness estimations to be made. It is well known however that different materials sputter at different rates and therefore it is difficult to obtain accurate measurements of individual layer thickness without extensive calibration. X-ray Diffraction (XRD) offers new possibilities for the characterization of thin films. Recently developed poly-capillary optics enable the generation of intense parallel beams of X-rays. This X-ray beam can then be used at grazing angles to provide a range of additional information on the nature of the thin film. This methodology allows accurate film thickness measurements to be obtained from monolayer to approximately 2000Å.This can be applied to multi-layer structures, providing an accurate measure of the individual layers enabling in-situ callibration of the sputter profile. The X-ray diffraction pattern also allows the polycrytalline phases within the film to be identified and quantified, providing additional support information for the chemical information provided by XPS. Variation of the diffraction pattern with grazing angle can also be used to obtain a measure of film thickness' of greater than 2000Å. This paper will demonstrate the enhanced characterization that can be achieved through the combined use and interpretation of the XPS and XRD data on a series of different materials and combined thin films.

3:20pm **AS2-MoA5 Photoelectron Spectroscopic Investigation of Interfaces and Thin Layers for Microelectronics: Composition and Chemistry as a Function of Depth**, ***R.L. Opila**, J.P. Chang, J. Eng, Jr., M. Du,* Bell Labs, Lucent Technologies **INVITED**

As dimensions shrink in microelectronics, the role of interfaces between materials becomes more important and the characteristic dimensions of microelectronics approach the escape depth of photoelectrons. Two strategies to examine thin layers and their interfaces will be described. First, the overlayer will slowly be deposited, the specimen will be transferred in vacuo, after which the photoelectron spectrum is recorded. This strategy has proven to be particularly useful in determining how metals react with polymers, which are being considered as low dielectric constant interlayers between conductors. Because it is desirable to use copper despite its poor adhesion, barrier layers of more reactive metals and their nitrides must be incorporated. We have successfully used photoelectron spectroscopy to study the chemistry that occurs between a series of low dielectric constant materials, including fluoropolymers and aerogels, and titanium, tantalum and their nitrides. The relative reactivity at the interface controls the morphology of the growing overlayer. The interface between the barrier metal and the copper seed layer has been studied. In another application of photoelectron spectroscopy, the composition and chemistry of oxide layers for use as gates in transistors or as dielectrics in capacitors have been studied. The thickness of the dielectric layer is comparable to the escape depth of the photoelectrons. Thus, we have been able to identify certain chemical states as those likely to act as defects in the electronic device. Moreover, using angle resolved photoemission, the composition of the dielectric overlayer has been determined as a function of depth for silicon oxynitrides and tantalum pentoxide. A maximum entropy algorithm to transform the angle resolved data to elemental and chemical depth profiles will be described. Reactions that occur at the buried interfaces between the dielectic and the underlying electrode will also be described.

4:00pm **AS2-MoA7 Analytical Conditions for Semi-Quantitative Auger Analysis of TaN**, ***C.F.H. Gondran,*** SEMATECH*; D.C. Nelsen,* SEMATECH, on assignment from Intel*; D.A. Hess,* Evans Texas

Historically, quantitative analysis of tantalum nitride (TaN) has been done by Rutherford backscattering spectroscopy (RBS), to avoid problems due to preferential sputtering effects seen in Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS). Recently tantalum (Ta) and TaN have emerged as leading candidates for barrier layers in advanced metalization schemes for next generation semiconductor devices. The small size of the features in these devices, as small 0.25 micron and shrinking, necessitates the development of a procedure to perform at least semi-quantitative analysis of TaNx films by a technique with significantly higher spatial resolution than RBS. In this paper the preferential sputtering effects seen in TaN by AES and XPS are characterized as a function of ion beam energy and film composition. This data is used to determine the most favorable analytical conditions for semi-quantitative AES analysis and develop an understanding of the limitations.

4:20pm **AS2-MoA8 Investigation of InP(110) Surface Damage Induced by Low Energy Ar and He Ion Bombardment**, ***Q. Zhao,*** The Chinese University of Hong Kong, P.R. China*; Z.W. Deng,* Tsinghua University, P.R. China*; R.W.M. Kwok, W.M. Lau,* The Chinese University of Hong Kong, P.R. China

High-resolution x-ray photoelectron spectroscopy (XPS) was employed to study the surface damage on n- and p-InP(110) caused by low energy ion bombardment in an ultrahigh-vacuum (UHV) system. The dynamic process of surface Fermi level shifting induced by ion bombardment as a function of ion dosage and ion energy was also measured. Two kinds of ion He@super +@ and Ar@super +@ at 10eV and 100eV energy with different ion dosages (from 10@super 12@ to 10@super 17@ ions/cm@super 2@) were chosen to investigate the performance of ion bombarded InP(110) surface. The results showed that the Fermi levels of both n- and p InP (110) surface moved to the midgap due to He@super +@ and Ar@super +@ ion bombardment, and ultimately pinned at about 0.95eV above the valence band maximum. More importantly, it was found that even at a bombardment energy of 10eV, ion fluence of 5x10@super 16@/cm@super 2@ was enough to cause an electrically active bandgap state density of 1x10@super 12@/cm@super 2@ which can detrimentally affect the device performance of the semiconductor.

4:40pm **AS2-MoA9 Phase Transformation of Cubic Boron Nitride Induced by Ion Bombardment**, ***B. Zheng,*** The Chinese University of Hong Kong, P.R. China, Hong Kong, P.R. China*; R.W.M. Kwok,* The Chinese University of Hong Kong, P.R. China*; M.Y.Y. Hui,* The Chinese University of Hong Kong, P.R. China, Hong Kong, P.R. China*; W.M. Lau,* The Chinese University of Hong Kong, P.R. China

The effects of argon ion bombardment on cubic boron nitride in the energy range of 50-1000eV were studied by electron energy loss spectroscopy with a field emission scanning Auger microscope (PHI 670), and by Auger and photoelectron emission. The microanalysis capability of the microscope allowed data collection from a (111) facet of a cubic boron nitride crystal, which largely increased the accuracy in the determination of the ion bombardment effects. Through monitoring the conversion of the electron energy loss features of cubic boron nitride to those of hexagonal boron nitride with an incident electron beam energy of 250eV, we determined the cubic to hexagonal phase transformation as a function of ion fluence and ion energy with a sub-monolayer sensitivity. We found that even at the low end of our bombardment energy range, the cubic to hexagonal phase transformation was still evident.

5:00pm **AS2-MoA10 Guided Ion-beam Studies of Low Energy Cu@super +@ and Cu@sub 2@@super +@ Ion Interactions with Ni(100)**, *S.L. Anderson, **A. Lapicki**, K.J. Boyd, M. Aizawa,* University of Utah

Low-energy (5-220 eV) Cu@super +@ and Cu@sub 2@@super +@ ions are deposited on Ni(100) under UHV conditions using the phase-space compressing ion beam deposition system at the University of Utah. The nature of the deposited Cu is determined by variable angle XPS and XAES. The disposition of the Cu deposits is explored as a function of ion energy and species. The Cu-Ni system exhibits stable surface and bulk alloys, and thus provides an interesting comparison to the C metal systems previously studied by ion beam methods (Ag/Ni, Cu/Mo). The influence of system thermodynamics and ion energy effects are examined via experiments and computer simulations.

Biomaterial Interfaces Group
Room 613/614 - Session BI-MoA
Protein Solid-Surface Interactions I

Moderator: G.U. Lee, Naval Research Laboratory

2:00pm **BI-MoA1 Formation of 2D Crystals of Proteins on Solid-Supported Lipid Bilayers Followed by AFM***, **A. Brisson**,* University of Groningen, The Netherlands, Netherlands*; I. Reviakine, W. Bergsma-Schutter, N. Govorukhina, S. Mazeres,* University of Groningen, The Netherlands

The possibility of assembling macromolecules or particles in a controlled manner on solid surfaces constitutes a central issue in the emerging field of nanotechnology. Methods for ordering proteins as 2D crystals or helical arrays at the level of lipid surfaces have received particular attention in molecular structure determination by electron crystallography. One of these methods, called the lipid layer crystallization method, uses the specific interaction between a protein and a ligand coupled to a l ipid molecule incorporated in a lipid monolayer at the air-water interface.@footnote 1@,@footnote2@,@footnote 3@ Our objective has been twofold: 1) to extend this strategy to the case of solid-liquid interfaces; 2) to develop an in situ method for following the formation of prot ein 2D crystals. Using Atomic Force Microscopy, both processes of formation of lipid bilayers on solid supports (SPB), and of protein 2D crystallization on SPB could be revealed in real time, in a natural aqueous environment, at sub-molecular resolution.@footnote 4@,@footnote 5@ Results will be presented on the crystallization of annexin V, an inhibitor of blood coagulation which binds specifically to negatively charged lipids, and will be compared to Electron Microscopy data of 2D crystals formed on lipid monolayers. This novel experimental approach offers exciting opportunities in basic science for investigating crystallization processes and provides an adequate technology for fabricating protein-containing biofunctional surfaces. @FootnoteText@ @footnote 1@Uzgiris, E.E. Kornberg, R.D., Nature 301 (1983) 125. @footnote 2@Brisson A. et al., J. Crystal Growth 196 (1999) 456. @footnote 3@Brisson, A. et al., in Crystallization of Proteins and Nucleic Acids, A Practical Approach, Oxford Univ. Pres (in press). @footnote 4@Reviakine, I., Bergsma-Schutter, W. Brisson, A., J. Struct. Biol. 121 (1998) 356. @footnote 5@Reviakine, I. Brisson, A., (submitted). .

2:20pm **BI-MoA2 Light Activated Affinity Micropatterning of Proteins***, **A. Chilkoti**, Z.-P. Yang, W. Frey,* Duke University*; T. Oliver,* Food and Drug Administration

Biomolecular patterning has diverse applications, which range from modulation of cell-substrate interactions in biomaterials and tissue engineering, to the fabrication of multianalyte biosensors, clinical assays, and genomic arrays. Motivated by these applications, we have developed a method to micropattern proteins on well-defined gold substrates, which we term light-activated affinity micropatterning of proteins (LAMP). LAMP is a multi-step patterning process: first, a gold substrate is functionalized with a binary mixture of 11-mercaptoundecanol and 16-mercaptohexadecanoic acid to provide a non-fouling, reactive self-assembled monolayer (SAM) template on gold. Next, the carboxylic acid end groups in the binary SAM are coupled to methyl @alpha@-nitropiperonyloxycarbonyl biotin succinimidyl ester (caged biotin ester) through a diamine linker. Deprotection of caged biotin by spatially-defined uv illumination at 350-360 nm reconstitutes biotin in the illuminated region, and subsequent incubation with streptavidin results in selective binding of streptavidin to regions that were previously deprotected. We have investigated and optimized LAMP by contact angle goniometry, ellipsometry, surface plasmon resonance, and X-ray photoelectron spectroscopy to maximize ligand density and pattern contrast. Micropatterning of streptavidin and an anti-biotin monoclonal antibody has been demonstrated with a spatial resolution of ~5 microns by imaging ellipsometry and confocal light microscopy of fluorophore-derivatized proteins. LAMP can be further extended to allow spatially-resolved micropatterning of multiple biomolecules by repeated cycles of spatially-defined deprotection, streptavidin incubation, followed by binding of the biotinylated moiety of interest.

2:40pm **BI-MoA3 Oriented Protein Binding via Silane-SAMs Using His-tagged Proteins***, C. Hoffmann,* University of Stuttgart, Germany*; H. Brunner, **G.E.M. Tovar**,* Fraunhofer Institute for Interfacial Engineering and Biotechnology, Germany

Oriented immobilization of proteins is a promising way of retaining protein activity on artificial surfaces.@footnote 1@ Modern protein engineering has already developed suitable tags for this purpose. Surface engineering is now required to provide complementary surfaces. We present experimental data on surface functionalization of silicon oxide surfaces using silane SAMs and the subsequent oriented binding of his-tagged proteins. We synthesized nitrilo-triacetic acid (NTA) silanes for direct attachment to silicon oxide surfaces, and NTA derivatives@footnote 2,3,4@ reactive to surfaces functionalized using epoxy terminated silanes. The stepwise surface functionalization and the binding capacitiy of the NTA surfaces for histidine peptides and his-tagged proteins has been investigated using XPS, MALDI-TOF-MS, contact angle measurements and in situ-ellipsometry. @FootnoteText@ @footnote 1@ Rao, S.V., Anderson, K.W., Bachas, L.G., Mikrochim. Acta, 1998, 128, 127-143. @footnote 2@ Dietrich, C., Schmitt, L., Tampe, R., Proc. Natl. Acad. Sci. USA, 1995, 92, 9014-9018. @footnote 3@ Sigal, G.B., Bamdad, C., Barberis, A., Strominger, J., Whitesides, G.M., Anal. Chem., 1996, 68, 490-497. @footnote 4@ Liley, M., Keller, T.A., Duschl, C., Vogel, H., Langmuir, 1997, 13, 4190-4192.

3:00pm **BI-MoA4 Complement Activation by IgM Immobilized on Methylated Silicon***, **P. Tengvall**,* Linkoping University, Sweden*; A. Askendal,* Linkoping University*; K.I. Lundström,* Linkoping University, Sweden

The activation of the complement system by IgM immobilized on methylated silicon was studied by ellipsometry/antibody techniques. The IgM coated surfaces were incubated in normal human- and depleated sera at 37Â°C up to 90 minutes, and the deposited amounts of characteristic proteins probed by antibodies. The results indicate, surprisingly, that the so prepared model surface activates the human complement in a manner independent of calcium, although via the classical pathway.

3:20pm **BI-MoA5 Theoretical and Experimental Studies of the Interaction of Water with Oligo (ethylene glycol) Terminated Self Assembled Monolayers***, R. Wang, H.J. Kreuzer,* Dalhousie University, Canada*; A.J. Pertsin, **M. Grunze**,* University of Heidelberg, Germany

The interaction of water with poly(ethylene glycol) and oligo(ethylene glycol) moieties in alkanethiolate SAMs is strongly dependent on the molecular conformation, lateral density and external electrical fields. In this contribution we will present ab initio quantum mechanical results and Monte Carlo Simulations on the ethylene glycol / water interaction and correlate them with vibrational sum frequency generation spectroscopic results of the OEG / water interaction,@footnote 1@ force distance measurements between neutral and charged AFM tips and OEG SAMs of different density,@footnote 2@ and single molecule force spectroscopy.@footnote 3@ @FootnoteText@ @footnote 1@M. Zolk, M. Buck, F. Eisert, M. Grunze, in preparation @footnote 2@K. Feldman, G. Habhner, N.D. Spencer, P. Harder, M. Grunze, JACS, submitted @footnote 3@F. Oesterheld and H. Gaub, New Journal of Physics 1 (1999), 6.1-6.11 3.

3:40pm **BI-MoA6 Protein Resistant Surfaces Based on Reactions of Thiol-Terminated Polyethylene Oxides with Gold***, **J.L. Brash**, Y.J. Du,* McMaster University, Canada

Gold is a relatively inert metal but has strong specific interactions with sulfur functions, particularly thiol. Thiols that contain bioinert or bioactive moieties (eg bioactive peptides containing a terminal cysteine) can thus be chemisorbed to gold films to provide correspondingly bioinert or bioactive surfaces. High surface densities of ligands should be possible due to the abundance of thiol binding sites in the surface. Thiolated gold surfaces thus have great potential in the design of biocompatible materials. We have used this approach in the development of a variety of surfaces based on:(1) suppression of non-specific protein adsorption, (2) selective/exclusive adsorption of a target protein from the contacting biological fluid. In the present work, surfaces have been developed consisting of HS-polyethylene oxides (HS-PEO, expected to minimize non-specific protein adsorption) chemisorbed to gold films deposited on polyurethane or silicon. PEOs of varying MW and architecture (linear, star) were reacted with mercaptoacetic acid to attach terminal thiol groups. HS-polypropylene oxides (HS-PPO) were used as controls, not expected to reduce protein adsorption. Chemisorption of the PEOs and PPOs to gold was verified by XPS. The adsorption of fibrinogen and albumin from buffer and plasma was studied by radioiodination methods. It was found that: (a) protein adsorption is low on all the modified surfaces and decreases with increasing molecular weight of the PEO, (b) with MeO as the terminal group at the free end of PEO, the suppression of protein adsorption is less than when OH is the terminal group, (c) chemisorbed PPO suppresses the adsorption of fibrinogen and albumin but not as effectively as PEO. In ongoing work we are investigating surfaces with heparin attached to the free chain end of chemisorbed PEO.

4:00pm **BI-MoA7 Protein Adsorption on Mixed Polyethylene Glycol/Methyl Terminated Alkane Thiol Self-Assembled Monolayers***, **T. Kim**, K.D. Hauch, J.W. Rogers, Jr.,* University of Washington

Polyethylene glycol(PEG) functionality has been used in many settings to resist protein adsorption.@footnote 1@ In this work, PEG and methyl terminated alkane thiols were used to form mixed self-assembled monolayers(SAM) on gold.@footnote 2@ These surfaces were used to study fibrinogen(Fg) adsorption. The molar percent of PEG thiol in the assembly solution was varied from 0-100% to vary the amount of PEG thiol on the surface. The mixed SAM's were examined with XPS. The atomic composition of the surfaces assembled from pure methyl thiol and pure PEG thiol agreed with expected values. An increase in ether bonds was seen as the PEG thiol ratio in the assembly solution was increased indicating an increase of PEG thiol in the mixed monolayer. The adsorption of I-125 labeled human Fg from dilute plasma (2 hr, 37 degrees Celsius) was measured. Fg adsorption on the SAM's ranged from 11-70 ng/cm^2, significantly lower than the control, polytetrafluorinated ethylene. The pure PEG thiol monolayer adsorbed 12 times less Fg than the control and 7 times less than the pure methyl SAM. We have demonstrated that the surface composition of the SAM is influenced by the composition of the assembly solution. Increased PEG thiol in the SAM reduced Fg adsorption with the pure PEG monolayer exhibiting the lowest values. Future work will include further surface characterization of the SAM's, adsorption studies with other proteins, and examination of choline or saccharide terminated thiols. @FootnoteText@ @footnote 1@ Lopez, G.P., et. al. Glow discharge plasma deposition of tetraethylene glycol dimethyl ether for fouling-resistant biomaterial surfaces. J. Biomed. Mater. Res. 1992, 26, 415-439 @footnote 2@ Ulman, A. Formation and Structure of Self-Assembled Monolayers, Chem. Rev. 1996, 96, 1533-1554

4:20pm **BI-MoA8 Properties of Oligo(ethylene glycol)- Terminated Alkanethiolates on Gold: Influence of Lateral Hydrogen Bonding***, **R. Valiokas**, S. Svedhem, S. Svensson, M. Östblom,* Linköping University, Sweden*; U. Gelius,* Uppsala University, Sweden*; B. Liedberg,* Linköping University, Sweden

An exhaustive study on properties of a class of oligo(ethylene glycol) (OEG)-terminated alkanethiolates on gold is presented. Contact angle goniometry, ellipsometry, infrared reflection-absorption spectroscopy, and X-ray photoelectron spectroscopy indicate formation of highly ordered self-assembled monolayers (SAMs), and the compounds containing amide moieties display lateral hydrogen bonding. The conformation of the OEG portion is shown to depend on the oligomer chain length and the lateral interactions, as evidenced by a different phase behavior of analogous OEG compounds which contain no amide group, as well as by using mixed SAMs of shorter and longer OEG chains. The assembly kinetics is found to be important in order to fine-tune the dominating phase of the SAMs. Furthermore, the thermal properties of the SAMs are investigated and temperature-dependent phase behavior is used to understand the nature of the conformational transitions of the OEG portion in relation to hydrogen bonding. Thus, the specifically introduced lateral interactions are shown to be not only a useful tool to improve the order and stability of the SAMs, but also to control conformational/functional properties of terminal groups which in this case are oligomers. Possible further modifications of such OEG SAMs and their bio-oriented applications are discussed.

4:40pm **BI-MoA9 1-Thiaoligo(Ethylene Oxide) SAMs: Biomimetic Matrix Structure Tuned via Hydrophilic Spacer Length & Packing Density***, **T. Petralli-Mallow**, D.J. Vanderah, C.W. Meuse, A.L. Plant,* National Institute of Standards and Technology

Interest in reconstituting transmembrane proteins into supported cell membrane mimics has led to development of novel tethering molecules. In order to introduce a flexible and fluid hydrophilic region at the proximal side of a supported lipid bilayer, oligo(ethylene oxide) moieties have been used as spacers between the sulfur and the alkane chain of alkanethiols. Our group has previously shown that the ethylene oxide moiety adopts a 7/2 helical conformation in self-assembled monolayers (SAM)s of both 1-thiahexa(ethylene oxide) (HS(EO)@sub 6@) decane and HS(EO)@sub 6@ octadecane on gold, indicating that the alkane chain is not the driving force for the helical conformation. Ethylene oxide structure may be controlled by packing density. For example, infrared analysis of mixed monolayers of HS(EO)@sub 6@-decane and phospholipids transferred from the air/water interface indicate that at low packing densities the EO region is disordered, but at higher packing densities the EO segment can assume the helical structure. For a series of decane-terminated 1-thiaoligo(ethylene oxide) SAMs with varying lengths of ethylene oxide spacers, infrared spectroscopy and sum frequency generation indicate that the conformation of the ethyleneoxide moieties may be controlled by their length. The conformation of the ethylene oxide segment is an extended all-trans chain in HS(EO)@sub 4@ SAM, a 7/2 helix in HS(EO)@sub 5-7@ SAM, and a less ordered conformation in the HS(EO)@sub 8@ SAM. The ability to control order via spacer length and packing suggests that HS(EO)@sub n@ SAMs may be successful platforms for biomimetic materials incorporating transmembrane proteins.

5:00pm **BI-MoA10 Reduction of Protein Adsorption on Polyethylene Glycol Covered Silica Surfaces***, **N.A. Alcantar**, T.L. Kuhl,* University of California at Santa Barbara*; E.S. Aydil,* University of California at Santa barbara*; J.N. Israelachvili,* University of California at Santa Barbara, US

Over the last decades, a large fraction of the scientific community has been dedicated to developing synthetic materials that can be used as implants or replacements for bones, organs, joints, tissues, skin, etc. These artificial materials must not only accomplish a specific function, but also be inert in the biological environment to which they are exposed. In general, the ability of a surface to reject proteins is a parameter used for determining its biocompatibility. Surfaces covered with polyethylene glycol (chemically (PEG, OH-(CH@sub 2@- CH@sub 2@-O)@sub n@-H) have been shown to be biocompatible as PEG enhances nonimmunogenecity, nonantigenicity and protein rejection. In order to produce a generic biocompatible surface coating, we have developed a direct method for grafting PEG onto amorphous activated silica surfaces or films. We first deposited an amorphous silica film by plasma enhanced chemical vapor deposition from SiH@sub 4@ and O@sub 2@ gases, which provides the flexibility to coat diverse materials with different shapes. These silica films were then activated by exposure to water plasma, thus increasing the number of hydroxyl groups on the surface. The silanols (Si-OH) on the resulting surface chemically react with the hydroxyl end of the PEG chain forming an ester bond, Si-O-C. The surface reaction was monitored using Attenuated Total Reflection Fourier Transform Infrared spectroscopy. Two representative fluorophore-labeled proteins were used in this study because of its relatively abundance in the blood stream. Measurements of protein absorption by fluorescence microscopy showed that the PEG coated surfaces significantly inhibit protein adsorption.

Electronic Materials and Processing Division
Room 608 - Session EM-MoA

Nitride Processing and Characterization

Moderator: J.S. Speck, University of California, Santa Barbara

2:00pm **EM-MoA1 GaN-Based Diode Structures for Optoelectronic Applications in the Near Ultraviolet Range of the Spectrum***, **D. Starikov**, I.E. Berishev, N. Badi, N. Medelci, J.-W. Um, A. Bensaoula,* University of Houston

We have previously reported that spectrally matched n-SiC and n-GaN-based Shottky barrier diode structures with semi-transparent Au electrodes can be employed for optoelectronic applications in the UV range of the spectrum. Both n-SiC-based and n-GaN-based structures indicated photosensitivity in the range down to 220 nm. The SiC- based structures exhibited optical emission in the avalanche mode at reverse bias down to 300 nm. The avalanche emission from the n-GaN-based samples was unstable and lasted only few seconds. In addition, high dark current and low thermal stability have been observed due to the absence of good ohmic contacts and satisfactory insulation, and poor mechanical and thermal stability of the gold layers. In this work Schottky barrier diode structures were fabricated on p-type GaN layers grown on sapphire using solid metal electrodes. The structures exhibit blue and wide-spectrum optical emissions at forward and reverse bias, respectively, and photo sensitive properties at no bias. Spectra of wide-spectrum optical emission and photo sensitivity measured through the sapphire substrate and 1.5 mm GaN film are matched in the range of 365-400 nm. The Lambertian radiant UV power of the blue emission is 466 mW at 22 V. Employment of wide-band gap oxide semiconductors In@sub 2@O@sub 3@ and SnO@sub 2@

for rectifying contact fabrication in our diode structures should extend the spectral range of our devices beyond 365 nm (the wavelength corresponding to the band gap of GaN) and improve their mechanical and thermal stability. We have incorporated these UV-transparent and electrically-conductive oxide semiconductor materials in our device structures. Our results from the various processing steps (patterning, etching, isolation and contact deposition), as well as from the diode structures characterization will be presented. Perspectives for applications of these structures in chemical sensors are discussed.

2:20pm **EM-MoA2 High Breakdown Voltage Au/Pt/GaN Schottky Diode***, J.I. Chyi, J.M. Lee, C.C. Chuo, G.C. Chi,* National Central University, Taiwan*;* ***G. Dang****, A.P. Zhang, X.A. Cao, M.M. Mshewa, F. Ren, S.J. Pearton,* University of Florida*; S.N.G. Chu,* Bell Labs, Lucent Technologies*; W.G. Wilson,* Charles Evans and Associates

Au/Pt/GaN Schottky diode rectifiers with a reverse breakdown voltage of -325V were demonstrated. The GaN sample studied in this work was grown on c-plane sapphire by low-pressure metalorganic chemical vapor deposition in a horizontal reactor. Ammonia (NH@sub 3@), trimethylgallium (TMG), and silane (SiH@sub 4@) were used as precursors and dopants, respectively. Two-step growth method was used to obtain GaN films with smooth surface. A low temperature GaN nucleation layer of about 220 nm was first grown at 460 °C after the substrate was heated at 1050 °C in hydrogen ambient for 10 minutes. Then the substrate temperature was raised to 1050 °C for the growth of the 1 µm-thick Si-doped (3E18 cm@super -3@) and 5 µm-thick undoped GaN layers. From the diode C-V measurement, the background doping of the undoped GaN is 1E16 cm@super -3@. The growth rate of high temperature GaN was 1.5 µm/hr, while that for the nucleation layer was about 0.3 µm/hr. TEM cross-sectional view of the sample shows that the growth interruption during the nitride growth reduces the dislocation density significantly. From the SIMS analysis, the concentrations of carbon, oxygen and hydrogen in the undoped layer are 2E17, 3E17, and 3E18, respectively. AFM roughness was around 1nm over 10x10 µm@super 2@.

2:40pm **EM-MoA3 Negative Electron Affinity and Electron Emission at Cesiated GaN and AlN Surfaces***,* ***C.I. Wu****, A. Kahn,* Princeton University

We present a systematic study of electron affinity and secondary electron emission at clean and cesiated surfaces of p-type GaN and (nominally n-type) AlN using ultraviolet and x-ray photoemission spectroscopy, and total yield spectroscopy. Clean and ordered 1x1 surfaces are prepared by nitrogen ion sputtering and annealing.@footnote 1@ The electron affinity, @chi@, is found equal to 3.3±0.2 eV and 1.9±0.2 eV for GaN and AlN surfaces, respectively, in agreement with previous results.@footnote 2,3@ The deposition of Cs reduces @chi@(AlN) by 2.6±0.3 eV, leading to true negative electron affinity (NEA), i.e. the vacuum level (E@sub vac@) is below the conduction band minimum (E@sub c@) at the surface. With the assist of a 1.2 eV initial downward band bending, effective NEA, i.e E@sub vac@ below the bulk E@sub c@, is achieved on p-GaN following the sequential adsorption of oxygen and deposition of cesium, which lowers @chi@(GaN) by 2.7±0.3 eV. The total yield, defined as the ratio of the total emitted current to the incident current, is strongly affected by the direction of band bending near the surface. For Cs/AlN, the upward band bending limits the total yield which reaches a maximum of 8 for incident electron energies of 600~900 eV and then decreases rapidly because secondary electrons excited deep in the solid are pushed back to the bulk by the field of the depletion region. On the other hand, Cs/GaN gives a maximum yield of 20 at higher incident electron energy (1200~1400 eV). This maximum is preserved up to much higher incident energy because the field of depletion region helps secondary electrons escape from the NEA solid.@FootnoteText@@footnote 1@ C.I. Wu, A. Kahn, E.S. Hellman and D.N.E. Buchanan, Appl. Phys. Lett., 73, 1346 (1998). @footnote 2@C.I. Wu and A. Kahn, Appl. Phys. Lett, 74, 546 (1999) @footnote 3@C.I. Wu and A. Kahn, J. Vac. Sci. Technol. B16, 2218 (1998) .

3:00pm **EM-MoA4 Inductively Coupled Plasma-Induced Etch Damage of GaN p-n Junctions***,* ***R.J. Shul,*** Sandia National Laboratories*; L. Zhang,* Sandia National Laboratories, US*; A.G. Baca, C.G. Willison, J. Han,* Sandia National Laboratories*; S.J. Pearton, F. Ren,* University of Florida

The fabrication of a wide variety of GaN-based photonic and electronic devices depends on dry etching through a p-n junction. Examples of these devices include laser diodes, light-emitting diodes, heterojunction bipolar transistors, p-i-n photodiodes and junction field effect transistors. The majority of dry etching methods used to pattern such devices rely on ion-assisted removal of the substrate material. Due to the relatively high bond energy (8.92 eV/atom) of GaN, the threshold ion energy for the onset of dry etching is typically on the order of 25 eV. Under conditions of both high ion flux and ion energies above this threshold, etch rates > 5,000Å/min are readily achieved for GaN in Inductively Coupled Plasma (ICP) or Electron Cyclotron Resonance (ECR) etch systems. However, under such conditions, the potential for plasma-induced damage is significant. Attempts to minimize such damage by reducing the ion energy or increasing the chemical activity in the plasma often results in a loss of etch rate or anisotropy which significantly limits critical dimensions and reduces the utility of the process for device applications requiring vertical etch profiles. It is therefore necessary to develop plasma etch processes which couple anisotropy for critical dimension and sidewall profile control and high etch rates with low-damage for optimum device performance. In this study, GaN p-i-n mesa diodes were formed by Cl@sub 2@/BCl@sub 3@/Ar etching at different ion energies and plasma fluxes. Reverse bias leakage currents were measured to evaluate damage created during plasma etch. Despite the increase in GaN etch rates observed with increasing ion energy and flux, damage was able to accumulate ahead of the etch front. Techniques to recover device performance will also be discussed. 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.

3:20pm **EM-MoA5 Schottky Diode Measurements of Dry Etch Damage in n- and p-type GaN***,* ***X.A. Cao,*** *A.P. Zhang, G. Dang, F. Ren, S.J. Pearton,* University of Florida*; R.J. Shul,* Sandia National Laboratories*; L. Zhang,* Sandia National Laboratories, US

N- and p- type GaN was exposed to Inductively Coupled Plasma (ICP)of N@sub 2@, Ar or H@sub 2@, as a function of high density source power(0-1400 W) and rf chuck power(20-250 W). For n-GaN there was a strong reduction in diode reverse breakdown voltage and an increase in forward and reverse currents, while for p-GaN the reverse breakdown increased. These results are consistent with creation of point defects with shallow donor nature that increase the conductivity of initial n-GaN or decrease the conductivity of initially p-GaN. Annealing at ~750 @super o@C under N@sub 2@ or removal of 500-600 Å of the surface essentially recovered the electrical properties of the plasma exposed GaN. For completed n-type mesa diode structures exposed to ICP Ar or Cl@sub 2@/Ar discharges, the low-bias forward currents increased by several orders of magnitude. The exposed surfaces became N@sub 2@-deficient in all cases, and both UV-ozone oxidation followed by dissolution of the oxide and annealing in N@sub 2@ were examined for restoration of the diode properties.

3:40pm **EM-MoA6 Process Development for Dry-etched Laser Facets on GaN***,* ***L. Zhang,*** Sandia National Laboratories, US*; R.J. Shul, G.A. Vawter, C.G. Willison, C.Y. Gao, J. Han,* Sandia National Laboratories*; S.J. Pearton,* University of Florida

With the rapid advance of III-N growth and processing technologies, GaN-based laser diodes (LDs) have been realized with continuously improved lasing thresholds and lifetimes. However, compared to their more mature arsenide and phosphide counterparts, the III-V nitride based LDs suffer from higher threshold current density and lower quantum efficiency. The reason for this is partly due to the lack of vertical profiles and sidewall roughness of the dry-etched laser facets in the III-V nitride structures, resulting in low mode reflectivity and high optical scattering loss. Therefore, it is essential to develop dry etch processes which yield anisotropic, smooth sidewalls. In this work, GaN etched sidewall profiles and morphologies are studied using an Inductively Coupled Plasma (ICP) reactor and will be compared to Reactive Ion Beam Etch (RIBE) results. Highly anisotropic profiles are expected in RIBE due to the acceleration of the ions through a series of grids located between the source and the sample as well as low pressure operation that reduces ion scattering. For BCl@sub 3@/Cl@sub 2@/Ar ICP chemistries, it was found that sidewall angles ranged from less than 70° to greater than 85° as a function of plasma chemistry, plasma density, ion energy, chamber pressure, and etch mask. The best ICP results were obtained using a photoresist mask, at 500 W ICP power, -150 V DC bias, 2 mTorr pressure, 32 sccm Cl@sub 2@, 8 sccm BCl@sub 3@, and 5 sccm Ar flow rate. 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.

4:00pm **EM-MoA7 Photo-Assisted RIE of III-V Nitrides in BCl@sub 3@/Cl@sub 2@/Ar/N@sub 2@***,* ***N. Medelci,*** *I.E. Berishev, D. Starikov, A. Bensaoula,* University of Houston*; M. Gonin, K. Fuhrer, A. Schultz,* Ionwerks

III-V nitrides are known as superior semiconductor materials for UV optoelectronic and high power, high temperature applications. However, these materials are extremely difficult to etch due to their high molecular bond strength. In order to address the device processing issue, reactive ion etching (RIE) and photo-assisted RIE processes were developed for boron nitride (BN) and gallium nitride (GaN) thin films. Our experiments show that optimum photo-assisted etching using a filtered Xe lamp occurs in Cl@sub 2@/Ar and BCl@sub 3@/Cl@sub 2@/N@sub 2@ chemistries for BN and GaN, respectively.@footnote 1-2@ Etch rates up to 324 (GaN) and 220 (BN) nm/min with smoother and cleaner etched surfaces were obtained with this process. In this work, we extend our studies to the AlGaN and InGaN ternaries. We also address some peculiarities observed in the previous work such as higher GaN etch rates for the UV-filtered Xe lamp, and lower GaN etch rates when a KrF excimer laser was used instead of the Xe lamp. To that end and to better understand these processes and characterize the photo-assisted effects, mass spectrometry determination of volatile species and optical emission spectroscopy (OES) identification of species in the plasma will be performed. The mass spectrometer used is a unique miniature time of flight prototype which employs orthogonal extraction, has a resolving power m/@Delta@m in excess of 500 and a detection limit of 10 ppm for all masses at a one second sampling rate. @FootnoteText@ @footnote 1@ A. Tempez, N. Medelci, N. Badi, D. Starikov, I. Berishev, and A. Bensaoula, "Photoenhanced reactive ion etching of III-V nitrides in BCl@sub 3@/Cl@sub 2@/Ar/N@sub 2@ plasmas", accepted for publication in J. Vac. Sci. and Technol. A (1999). @footnote 2@ N. Medelci, A. Tempez, I. Berichev, D. Starikov and A. Bensaoula, "Photo-assisted RIE of GaN in BCl@sub 3@/Cl@sub 2@/N@sub 2@", Mat. Res. Soc. Symp. Proc. (1999) (submitted).

4:20pm **EM-MoA8 Effect of N@sub 2@ Discharge Treatment on AlGaN/GaN HEMT Ohmic Contact Using Inductively Coupled Plasma**, ***A.P. Zhang****, G. Dang, X.A. Cao, F. Ren, S.J. Pearton,* University of Florida; *J.M. Van Hove, P.P. Chow, R. Hickman, J.J. Klaasen,* SVT Associates

Due to the excellent thermal stability and large energy band-gap of GaN based material system, AlGaN/GaN based high electron mobility transistors (HEMTs) have an excellent potential for high temperature and high power applications. The conventional low resistance n@super +@-cap layer structure used to reduce parasitic resistances in GaAs technology is generally not applied in nitride devices as it is difficult to perform the gate recess step. This is due to the high chemical stability of GaN which makes wet etching very difficult except at high temperatures or under optical stimulation. Mochi has demonstrated that an exposure of Ar or N@sub 2@ discharge to ohmic contact region before the metal deposition showed an improvement of contact resistance. However a systematic study of plasma energy and time has not been performed yet. In this work, we investigate the contact resistance by varying the chuck power from 10-60W and ICP discharge power from 100 to 700W and plasma exposure time from 40 to 80 sec. The effect of anneal temperature was also studied. The ion bombardment sample showed two order of magnitude lower contact resistance than that of un-treated sample. Auger and AFM were also used to analyze the effect of ion bombardment. The photoresist was also optimized for the plasma treatment.

4:40pm **EM-MoA9 In-Situ Plasmas Diagnostics for the Etchings of AlGaN/GaN Heterostructures**, *H.S. Kim,* SungKyunKwan University, South Korea; ***G.Y. Yeom****,* SungKyunKwan University, South Korea, Korea; *J.W. Lee, T.I. Kim,* Samsung Advanced Institute of Technology, South Korea

AlGaN/GaN heterostructures have been widely used to form the various devices such as field effect transistor(FET), photodiode, bipolar transistor(BT), light emitting diode(LED), and laser diodes(LD). High etch rate of the full structure and reliable etch end point detection are required to form a device by dry etching. In the previous work, plasma characteristics during the GaN etching have been reported using a quadrupole mass spectrometry (QMS) and an optical emission spectroscopy (OES) and an etch mechanism of GaN by Cl@sub2@-based plasmas has been proposed from the detection of etch products. In this study, GaN, AlGaN, and AlN grown on sapphire, and AlGaN/GaN heterostructures were etched using inductively coupled Cl@sub2@/BCl@sub3@ plasmas. Etch rates of GaN were higher than those of AlGaN for the Cl@sub2@ rich plasmas. The increase of Al composition in the AlGaN decreased the etch rate of heterostructures regardless of plasma conditions. These differences in the etch rate could be reduced by the increase of BCl@sub3@ to Cl@sub2@ gas and the decrease of the pressure. The plasma characteristics and their relations to etch rates were investigated using in-situ plasma diagnostics such as QMS and OES. Finally, the etch end point of an AlGaN/GaN heterostructure and a LD structure could be estimated by the monitoring an Al-containing optical emission line. Detailed data will be shown in the presentation.

Flat Panel Displays Topical Conference
Room 604 - Session FP-MoA

Luminescent Thin Films

Moderator: P.H. Holloway, University of Florida

2:00pm **FP-MoA1 Critical Issues Related to Processing and Properties of Laser Deposited Luminescent Oxide Thin Films**, ***R.K. Singh****, K.G. Cho, D. Kumar, P.H. Holloway,* University of Florida **INVITED**

The performance of the powder-based field emission display devices can be improved significantly by using thin film phosphors due to their higher lateral resolution, better thermal stability, reduced outgassing, and better adhesion to the solid surfaces. A variety of growth techniques such as evaporation, spray pyrolysis, sputtering, metal organic chemical vapor deposition, and pulsed laser deposition, are employed for the fabrication of thin film phosphors. The pulsed laser deposition (PLD) technique is emerging as one of the most convenient techniques to fabricate complex thin films since it offers numerous advantages, including convenient reproduction of target stoichiometry onto the films, low contamination level, high deposition rate, atomically sharp step coverage, thickness control. However, the biggest hindrance in the use of thin film phosphors is their low brightness and efficiencies in comparison to those of bulk powder phosphors. In this talk, we will discuss some of the critical issues related to processing and properties of laser deposited Eu-activated yttrium oxide (Eu:Y @sub 2@ O @sub 3@) luminescent thin films. We will also present our results showing how brightness and stability can be improved significantly by changing microstructure, orientation, and crystallinity of Eu:Y@sub 2@O@sub 3@ films by changing the processing parameters during pulsed laser deposition. A theoretical model will be presented to account for the increase in brightness with an increase in film roughness which has been found to be a key parameter determining the light piping effect.

2:40pm **FP-MoA3 The Effect of Carbon Deposit on Electron Beam Degradation of Oxide Thin Film Phosphors**, ***C. Kondoleon****, B.L. Abrams, J. Thomes,* University of Florida; *P. Rack,* Rochester Institute of Technology; *V. Krishnamoorthy, P.H. Holloway,* University of Florida

The cathodoluminescence (CL) brightness and spectral distribution from thin film Ta@sub2@Zn@sub3@O@sub8@ has been studied as a function of electron dose. Thin films of Ta@sub2@Zn@sub3@O@sub8@ were prepared by sputtered deposition followed by rapid thermal annealing (RTA). Under bombardment by 2keV electrons, the films produce a blue luminescence with a dominate wavelength of 386nm. These films were exposed to residual vacuum gas dominated by H@sub2@ and H@sub2@O at pressures ranging from 10@super-8@ Torr to 10@super-6@ Torr with <5% loss in CL brightness. However when hydrocarbons from colloidal graphite paint was introduced and raised the base pressure of the vacuum from 1 x 10@super-8@ Torr to 8 x 10@super-8@ Torr, the CL brightness was degraded to 5% of its original value after approximately 4 hours at 2.7 x 10@super-4@ A/cm@super2@ (corresponding to a dose of 3.9 C/cm@super2@). The electron beam stimulated degradation since when the beam was off, degradation stopped. In addition, on some samples the electron beam was blocked by a Cu grid over the surface and degradation only occurred when the electron beam struck the surface. Auger analysis showed a thick layer of carbon. It is speculated that the electron beam cracked hydrocarbons, resulting in deposition of a carbonaceous layer which attenuated primary electrons and absorbed luminescent photons. The significance of this phenomena in field emission displays will be discussed. This work is supported by DARPA Grant MDA 972-93-1-0030, through the Phosphor Technology Center of Excellence.

3:00pm **FP-MoA4 Blue Luminescence Properties of Zinc Oxide Doped with Low Concentration of Tungsten**, ***J.B. Sobti****, V. Bhatia, P.M. Babuchna, M.H. Weichold,* Texas A&M University

Research in developing high quality thin film phosphors for field-emission displays (FEDs) has gained momentum over the last decade. From the aspect of low voltage applications, cost and durability, efficient red and gren phosphors are now available. However, phosphors for blue light still need improvement. An investigation conducted at Texas A&M University showed that tungsten doped zinc oxide (ZnO:W) emits blue light at 490 nm when excited at 300V.@footnote 1@ Results for this phosphor preparation, its luminescence and material characterizations, and potential use in fabricating a FED are prsented in this paper. Using ion mill, thin films of ZnO and W were co-deposited. The films with varying W concentrations (10%, 30%, and 50%) were annealed at 450°C, 650°C, and 850°C for 4, 8, and 12hrs in the presence of argon and oxygen. Luminescent characterization of these films indicated that phosphor having 10% W, annealed at 850°C for 12 hrs. in pure argon emitted the brightest blue light.@footnote 2@ Continuing research involves studying the effect of even lower W concentrations under above-mentioned conditions. Radiance data for ZnO:W phosphor will be measured and compared with the efficiencies of other blue phosphors. X-ray diffraction studies and infrared spectroscopy of the films showed formation of zinc tungstate (ZnWO@sub 4@), which has been reported to exhibit photoluminescence at 490 nm. This led us to conclude that ZnWO@sub 4@ is the source of blue light from our phosphor.@footnote 3@ This paper also presents results from Stokes shift measurements to understand mechanisms for blue light emission. Research is underway in determining a material chemically compatible with the phosphor to form anode lines for the display. Results from this research will also be reported. @FootnoteText@ @footnote1@Technology Disclosure to TAMU Technical Licensing Office (1993). @footnote 2@J. B. Sobti et al, April 1998, AVS Texas Chapter meeting. @footnote 3@J. B. Sobti et al, Spring, 1999, MRS meeting.

3:20pm **FP-MoA5 Progress in TFEL Technology***, **S.-S. Sun**,* Planar Systems, Inc. **INVITED**

This paper will review the basic operation of inorganic TFEL displays. Recent progress in monochrome and color TFEL phosphors including the new efficient blue TFEL phosphor will be presented. The application of these improved phosphors in direct view and active-matrix TFEL displays, both monochrome and color versions, will be described.

4:00pm **FP-MoA7 Multicolor Emitting TFEL Devices using Ga@sub 2@O@sub 3@ Phosphors Co-doped with Mn and Cr***, T. Minami, **T. Nakatani**, T. Miyata,* Kanazawa Institute of Technology, Japan

This paper introduces newly developed TFEL devices consisting of Mnand Cr-co-doped Ga@sub 2@O@sub 3@ phosphor thin-film emitting layers combined with a thick BaTiO3 ceramic sheet insulating layer. The co-doping effects of Mn doped into Ga@sub 2@O@sub 3@:Cr thin films and Cr doped into Ga@sub 2@O@sub 3@:Mn thin films on their electroluminescent properties have been investigated. Ga@sub 2@O@sub 3@:Mn,Cr phosphor thin films were prepared using a solution coating technique. The Mn and Cr dopant contents (Mn/(Mn+Ga) and Cr/(Cr+Ga) atomic ratios) were varied from 0 to 20 atomic%. In order to improve the EL characteristics, all deposited Ga@sub 2@O@sub 3@:Mn,Cr phosphor thin films were post-annealed in an Ar atmosphere for 1 h at 1020@super o@C. The emission from Ga@sub 2@O@sub 3@:Mn,Cr TFEL devices was more strongly dependent on the Cr content than on the Mn content doped into the phosphor emitting layers. A high luminance above 100 cd/m@super 2@ was obtained in all TFEL devices using Ga@sub 2@O@sub 3@:Mn,Cr thin films co-doped with a Cr content from 0 to 20 at.% and a Mn content of 0.3 at.% when driven at 1 kHz. The emission color from these Ga@sub 2@O@sub 3@:Mn,Cr TFEL devices changed from green to red emission as the co-doped Cr content was varied from 0 to 20 at.%. In addition, the emission color changed from green to red as the applied voltage was increased. Thus, Ga@sub 2@O@sub 3@:Mn,Cr TFEL devices would be useful in color indicators and displays, with color controlled by the applied voltage.

4:20pm **FP-MoA8 Effect of Ce@sub 2@O@sub 3@ and Ag/Cu Codoping on the Brightness and Efficiency of RF Magnetron Sputtered ZnS:TbOF Alternating Current Thin Film Electroluminescent Displays***, J.P. Kim, **D.J. Moorehead**, K.E. Waldrip, B. Speck, M. Davidson,* University of Florida*; P.H. Holloway,* University of FLorida*; Q. Zhai,* University of Florida

ZnS:TbOF has shown promise as a green electroluminescent phosphor, but it still lacks the performance necessary to incorporate it into a commercially viable ACTFEL device. Many codopants have been shown to improve the performance of such devices. This study reports the results of Ce@sub 2@O@sub 3@ and Cu/Ag codoping on the brightness and efficiency of ZnS:TbOF thin film EL devices. As-deposited Ce codoped ZnS:TbOF films showed no significant change in brightness. Annealing of low Ce concentration half-stack (no top dielectric) devices improved EL brightness by 65% over the best undoped samples. Scanning electron microscopy shows no significant morphology changes in annealed films. Ag/Cu codoping did not dramatically effect the brightness of as-deposited films, but there were significant improvements in BV characteristics of annealed samples. Half-stack data show a much sharper turn-on and B20 improvement from 32 cd/m2 to 70 cd/m2. Samples annealed at high-temperature (850°C) demonstrated severe degradation in brightness and efficiency, while SEM micrographs show that grain size significantly decreased, possibly due to precipitation of another phase.

4:40pm **FP-MoA9 A Comparison of the Short Wavelength Performance of ZnS and SrS Thin-Film Electroluminescent Devices via a Rare Earth Doping Study***, P.D. Keir, **C.M. Maddix**, B. Baukol, J.F. Wager, B.L. Clark, D.A. Keszler,* Oregon State University

The short wavelength electroluminescent (EL) performance of SrS and ZnS phosphors for thin-film EL flat-panel display applications is compared. This is accomplished by measuring the EL spectra of ZnS and SrS EL devices doped with various rare earth luminescent impurities: Dy, Er, Ho, Tb, and Tm. All of the SrS EL devices tested have more intense EL emission at short wavelengths than corresponding ZnS EL devices. Additionally, all of the SrS EL devices operate at smaller average phosphor fields. The superior EL performance of SrS appears to be due to a hotter electron distribution and to the presence of positive space charge in SrS EL devices. The ZnS devices show a distinct EL cut-off at ~440-460 nm. This is attributed to an inadequately heated electron distribution which is unable to excite high energy transitions in the luminescent impurity. Collectively, these results indicate that efficient blue emission from a ZnS phosphor is unlikely.

5:00pm **FP-MoA10 Role of Cations and Anions in Donor Doping of ZnS:Mn Thin Film Electroluminescent Phosphors***, **K.E. Waldrip**, J.S. Lewis, III, Q. Zhai,* University of Florida*; M. Puga-Lambers, M. Davidson,* University of Florida, Microfabritech*; P.H. Holloway,* University of Florida*; S.-S. Sun,* Planar Systems, Inc.

Alternating current thin film electroluminescent ZnS:Mn phosphors have been deposited by RF magnetron sputter deposition on glass substrates coated with indium tin oxide (ITO) transparent conductor and an alumina-titania (ATO) composite dielectric. A co-dopant was introduced by an ex-situ diffusion method. The top dielectric and contact layers were deposited to complete the device. Control samples were processed exactly the same, with the exception that the co-dopants were not introduced. Co-doping ZnS:Mn thin film electroluminescent phosphors with potassium chloride resulted in a 50% increase in brightness and efficiency (150fL, 1.9L/W vs. 100fL, 1.3L/W), a 5% increase in threshold voltage, and an improvement in brightness vs. voltage stability. Electrical analysis revealed increases in the amount of transferred charge, leakage charge, internal phosphor field, and in the overall symmetry of the electrical characteristics with respect to applied voltage pulse polarity with KCl co-doping. The observations to date of the improved performance in co-doped ZnS:Mn can be explained by a donor doping mechanism in which chlorine acts as the shallowest and most abundant donor in the phosphor film. Interstitial potassium also behaves as a donor, and the theory rests on the assumption that there are more activated donors than acceptors. The purpose of the work presented here is to elucidate the role of the cation and the anion in the improved performance of co-doped ZnS:Mn phosphors. KF, KCl, KBr, LiCl, NaCl, ZnCl@SUB 2@ and K@SUB 2@S were tested as dopants to deconvolute the roles of the anion and the cation. The brightness and efficiency vs. voltage and threshold voltage for each sample will be reported against the control samples. SIMS and XTEM, as well as spectral distribution and electrical analysis will also be presented and correlated with the donor doping theory.

Magnetic Interfaces and Nanostructures Technical Group
Room 618/619 - Session MI+VM+AS-MoA

Magnetic Recording: Media and Heads

Moderator: D.E. Fowler, Maxtor Corporation

2:00pm **MI+VM+AS-MoA1 Spectro-Microscopy of Magnetic Materials Using Polarized Soft X-Rays***, **J. Stohr**,* IBM Almaden Research Center **INVITED**

The talk discusses the motivation for and challenges of obtaining magnetic information for ferromagnetic and antiferromagnetic systems on a length scale below 100nm. It reviews the principles of linear and circular x-ray magnetic dichroism spectro-microscopy and presents state-of-the-art results (20nm resolution) obtained with a dedicated soft x-ray photoelectron emission microscope (PEEM) installed on the Advanced Light Source (ALS) at Lawrence Berkeley National Laboratory. Results include studies of the antiferromagnetic domain structure at the surface of LaFeO3(100), NiO(100) and polycrystalline NiO and the ferromagnetic domain structure in hard/soft magnetic tunnel junctions. Future plans to reach a spatial resolution below 10nm will also be discussed.

2:40pm **MI+VM+AS-MoA3 Micromagnetic Properties and Recording Performance in High Density Magnetic Recording Media***, **T. Suzuki**, G. Lauhoff,* Toyota Technological Institute, Japan **INVITED**

In order to increase areal recording density, much effort has been made to improve magnetic charactreristics and microstructure in magnetic recording media. In order for decreasing noise and for realizing a sharp transition between written bits, an inter-granular exchange coupling must be lowered, which enhances a thermal instability of magnetization. Given this conditions, it is vitally important to understand the role of magnetic activation volume or magnetic coupled region in conjunction with micromagnetics, which plays a key role in noise mechanisms. The present study is to discuss activation volume in longitudinal magnetic recording media of various types including CoCrPtTa thin-films and granular-type recording media. The activation volume is evaluated based on the time decay of magnetization at a certain field. A novel method to define the activation volume is proposed. The Barkhausen volume is estimated through the field-sweep-rate dependence of coercivity. It is found that the activation volume, which is of the order of 10@super -18@ cm@super -3@, decreases with applied field, then levels off, and starts increases at fields beyond coercivity. This trend is found for all the high density recording media of CoCrPtTa and granular-type media under consideration. The recording noise is found to be closely related to activation volume. Measurments of @delta@M curves suggest that lesser the granular-exchange-coupling is, the smaller the activation volume becomes.

3:20pm **MI+VM+AS-MoA5 Sub 50 nm Planar Magnetic Nanostructures Fabricated by Ion Irradiation***, T. Devolder, **C. Chappert**,* IEF/Université Paris Sud, France*; Y. Chen,* L2M Bagneux/CNRS, France*; H. Bernas,* CSNSM/Université Paris Sud, France*; J.-P. Jamet, J. Ferré,* LPS/Université Paris Sud, France*; E. Cambril,* L2M Bagneux/CNRS, France **INVITED**

Areal density enhancement is a major challenge in magnetic recording. Near field magneto-optical techniques are one fast-developing attempt to respond. At bit density values above 65 Gbits/in@super 2@, a most drastic requirement will be to write stable bits with nanometer wall jaggedness, at very precise locations on the disk. Patterned media could be a promising response to this problem.@footnote 1@ However, surface roughness, and polarization dependent effects due to abrupt changes in optical index, will likely deteriorate the signal to noise ratio. Through interface mixing, light ion (He+) irradiation can modify in a precisely controlled way the magnetic properties of multilayers, with negligible change of surface roughness and optical indices. In (Co/Pt) multilayers with perpendicular easy magnetization axis, the anisotropy decreases with irradiation, which first reduces the coercive force, then induces in-plane magnetization. Patterning only the magnetic properties can then be obtained by irradiation through a lithographic PMMA resist mask.@footnote 2@ Using SiO@sub 2@ masks, we have fabricated regular arrays of such irradiation-patterned nanostructures with sizes down to 30 nm. Different configurations such as hard (resp. soft) nanostructures in soft (resp. hard) media have been obtained and characterized using far field magneto-optical microscopy. Special attention has been devoted to the study of the transition zone between irradiated and protected areas, and its effect on magnetization reversal. The technique may be a powerful tool for ultrahigh density magnetic recording applications. @FootnoteText@ @footnote 1@ S. Chou et al., Data Storage 35 (1995). @footnote 2@ C.Chappert et al., Science 280, 1919 (1998).

4:00pm **MI+VM+AS-MoA7 Crystallographic Texture and Stress in Co-Based Magnetic Recording Media and Underlayers***, **B.M. Clemens**, G. Khanna,* Stanford University **INVITED**

The magnetic and recording properties of Co-based media are a strong function of crystallographic texture and stress in the media layers, which are in turn strongly influenced by the texture and stress of the Cr underlayer. The anisotropy in strain and the distribution of c-axes in the hcp Co alloy media can determine the magnetic hysteresis anisotropy through magnetostrictive and magnetocrystalline effects. The processing conditions and mechanical texture grooves in the NiP/Al substrate strongly influence the microstructural and mechanical properties of the Cr and Co films. We report x-ray studies of the texture and strain in Cr and Co-based films sputter deposited over a range of temperatures and substrate biases on smooth and mechanically textured substrates. All films showed an in-plane compressive stress. The magnitude of the stress in Cr and Co films grown without a substrate bias decreases with decreasing growth temperature, consistent with thermal mismatch stress. The stress in the Cr films grown with a -300V bias was greater than that of unbiased films, and independent of growth temperature. This suggests that the bias-induced stress is close to the yield stress of the film. However, the biased Co films show a decrease in compressive stress with decreasing temperature. For mechanically textured substrates, the stress measured in the direction perpendicular to the texture grooves was less compressive relative to the parallel direction in both Cr and Co. However, the stress anisotropy vanishes in smooth substrates. A simple strain relaxation model is used to explain the observed Cr stress values in the textured disks. The anisotropic strain in the Cr may also account for the observed preferential alignment of Co c-axes along the grooves. Calculation of the magnetoelastic and magnetocrystalline energies predicts that Co stress anisotropy and the preferential alignment of Co c-axes along the grooves both contribute to the observed hysteresis anisotropy.

4:40pm **MI+VM+AS-MoA9 Noise in GMR Recording Heads***, **H.T. Hardner**, M.B. Hurben,* Seagate Technology **INVITED**

Magnetoresistive sensors exploit a close coupling between magnetization and resistance to convert changes in magnetic field to an electrical signal. Thus, the enhanced sensitivity of the giant magnetoresistive (GMR) materials to magnetic field is accompanied by larger electrical noise due to magnetization noise. A magnetic contribution to 1/f noise originates in thermal fluctuations in magnetization. This is a concern for sensors intended for low frequency applications rather than for magnetic recording heads due to the very high frequencies at which the heads operate. However, discrete steps in the resistance can also appear due to large discrete changes in domain structure. When these steps occur as a continuous magnetic signal is applied to the device they are called Barkhausen noise. In small enough devices discrete magnetoresistive steps can be observed even at fixed magnetic field. While the sensitivity of the resistance to changes in magnetization is proportional to the magnetoresistance, the propensity for complex domain structure with fluctuations between multiple metastable states varies by material, processing, and design. The suppression of these fluctuations to create a device with a single stable magnetization state is a key goal in the design and manufacture of magnetoresistive recording heads. This talk will provide some brief background on how recording heads are stabilized as well as an overview of resistance noise data from GMR devices including comparisons of different materials and the use of resistance noise measurements to study domain structure. Recent results on resistance noise in spin-valve recording heads both at the finished stage and during wafer processing will be presented along with discussion of how a detailed study of electrical noise can help identify stability problems. Analysis of both time and frequency domain data will be considered.

Manufacturing Science and Technology Group
Room 611 - Session MS-MoA

Ultra-Clean Society and Contamination Free Manufacturing

Moderator: A.C. Diebold, Sematech

2:00pm **MS-MoA1 Highly Reliable Ultra Thin Gate Oxide Grown using Water Vapor Generator***, **O. Nakamura**, T. Ohkawa, M. Nakagawa, Y. Shirai,* Tohoku University, Japan*; K. Kawada, N. Ikeda, Y. Minami, A. Morimoto,* Fujikin Incorporated, Japan*; T. Ohmi,* Tohoku University, Japan **INVITED**

High-reliability ultra thin oxide film is required for future ULSI manufacturing, where perfect uniformity and very high yield in volume production of large diameter wafers era must be guaranteed. In case of wet oxidation, water vapor is most commonly generated by burning H@sub 2@ in O@sub 2@ ambient. So, this torch-type has a potential problem of particle contamination of the water due to the micro-powder from the quartz combustion nozzle. In order to obtain wet ambient without contamination, we have developed a new Water Vapor Generator (WVG) using catalytic reactor. Additionally, the WVG can generate H2O from the vacuum to the high-pressure condition. This WVG is expected to be used in various processes where water vapor is needed.In this presentation, we will demonstrate a new gate oxidation process to form high-reliability ultra thin gate oxide at low temperature with highly concentrated H@sub 2@O using WVG system. For example, for substrate injection, the 50% Q@sub BD@ values of conventional dry oxides (900@super o@C) and advanced wet oxides formed at the low temperature using highly concentrated moisture (90% H@sub 2@O/Ar, 750@super o@C) are 9.5 C/cm@super 2@ and 70 C/cm@super 2@, respectively. For gate injection, the 50% Q@sub BD@ values of conventional oxides and advanced oxides are 6.5 C/cm@super 2@ and 25 C/cm@super 2@, respectively. Moreover, we will discuss the influence of oxidation ambiences such as surplus O@sub 2@ and H@sub 2@ ambience and oxidation temperature for electrical characteristics. In conclusion, ultra thin gate oxide using WVG has high breakdown strength under electrical stress. A newly developed oxidation is effective to grow a tunnel oxide for flash memory, which is operated under high electric field.

2:40pm **MS-MoA3 High-integrity Ultra-thin Silicon Nitride Film Grown by Plasma Nitridation of Silicon Surface at Low-temperature for Giga Scale Devices***, **K. Sekine**, Y. Saito, M. Hirayama, T. Ohmi,* Tohoku University, Japan

The progress of MOSLSI technology has been based on the shrinking of MOSFET's. Along with downsizing MOSFET's for more than 25 years, the gate oxide equivalent thickness of MOSFET's has continued to be reduced. Since the invention of MOS device, thermally grown silicon oxide, the prevailing gate dielectric for Si based MOS devices, processes remarkable electrical properties that are unmatched by other materials. However, transistor scaling is driving gate oxide equivalent thickness to 3 nm and below, when direct tunneling current becomes significant. Ultra thin silicon oxide below 3 nm is not expected to be robust enough for future transistor gate dielectric application. In order to continue downsizing MOSFET's, thermally grown silicon oxide will be replaced by higher dielectric-constant films, for example Ta@sub 2@O@sub 5@ and Si@sub 3@N@sub 4@. A radial line slot antenna (RLSA) high-density plasma system can form high-integrity silicon nitride film at a temperature of 400 °C. We focus attention on electrical properties of ultra-thin silicon nitride films grown by radial line slot antenna high-density plasma system at a temperature of 400°C as an advanced gate dielectric film. The results show low density of interface trap and bulk charge, lower leakage current than jet vapor deposition silicon nitride and thermally grown silicon oxide with same equivalent oxide thickness. Furthermore, they represent high breakdown field intensity, almost no stress-induced leakage current, very little trap generation even in high-field stress, and excellent resistance to boron penetration and oxidation.

3:00pm **MS-MoA4 Generation of Positively Charged Particles at an Anode and Transport to Device-wafers in a Real rf-plasma Etching Chamber for Tungsten Etch-back Process***, **T. Moriya**, N. Ito, F. Uesugi,* NEC Corporation, Japan*; Y. Hayashi, K. Okamura,* NEC Kyushu, Ltd., Japan

In this paper, it is clarified that the particles, flaked off from a grounded anode of parallel-plate rf plasma etching equipment, have positive charges. Moreover, the particles transport from the anode to the device-wafer on the cathode with keeping away from bulk plasma. In previous papers, we have reported that, in the middle space between the two electrodes, many particles were observed at the timing of the rf power off, and seemed to be drawn to the wafer with the residual negative self-bias voltage.@footnote 1,2@ To clarify the polarity of charge and the transport path of particles, the appearances and the trajectories in relation to the workings of the etching equipment are studied in detail both near the anode and the device-wafer on the cathode. Surprising results are obtained. Near the grounded anode, a few particles appear constantly and have parabolic trajectories with open upward in the duration of rf power, and many particles appear and have sharply curved trajectories from the anode to the chamber wall at the rf power off. On the other hand, near the wafer on the cathode, almost all particles appear at the rf power off and are drawn from the chamber wall to the wafer. These results mean the particles are reflected by the plasma potential, and they transport from the anode to the wafer with keeping away from the residual bulk plasma under the existence of attractive force between the particles' positive charge and the residual negative charge of the wafer. @FootnoteText@ @footnote 1@F. Uesugi, et al., J. Vac. Sci. Technol. A 16, 1189 (1998).@footnote 2@N. Ito, et al., J. Vac. Sci. Technol. B 16, 3339 (1998).

3:20pm **MS-MoA5 Standardization of the Method to a Moisture Concentration in Hydrogen Chloride Gas with Diode Laser Absorption Spectrometry***, **Y. Ishihara**,* UC Standardization Committee, Japan*; Y. Sakakibara,* NTT Advance Technology Corporation, Japan*; Y. Kunii,* Kokusai Electric Co., Ltd., Japan*; K. Hasumi,* Hitachi Tokyo Electronics Co., Ltd., Japan*; I. Matsuda,* Showa Denko K.K., Japan*; N. Miki,* Ultraclean Technology Research Institute, Japan*; A. Ohki,* Oosaka Sanso Kogyo Ltd., Japan*; Y. Shirai,* Tohoku University, Japan

A standard method is proposed, using diode LASER absorption spectroscopy, to measure the moisture (H@sub 2@O) in hydrogen chloride (HCl) gas at concentrations between 100 ppb to 0.1%. This standard is laid down to measure trace H@sub 2@O in HCl at point of use. In this standard, HCl with H@sub 2@O of unknown concentration (sample gas) is introduced into a laser absorption spectrometer which is kept at reduced pressure. Measurement is performed in the range of 1370 nm to 1389 nm in wavelength, and the second-derivative absorption intensity of H@sub 2@O is calculated. Using the second-derivative absorption intensity and pre-defined calibration curve, the H@sub 2@O concentration is determined. The determination limit, which was defined as 3 times of the standard deviation of the second-derivative intensity, was found to be 100 ppb when a program for noise cancellation was employed. For verification of calibration curve, calibration curves which were prepared at different timings at different places by different people showed good agreement of over 95%. Moreover, it is proved that calibration curve of H@sub 2@O in HCl can be substituted by that of H@sub 2@O in N@sub 2@ which is corrected with a correction coefficient.

3:40pm **MS-MoA6 Gas Distribution System Using an Advanced Flow Controller***, **M. Nagase**, O. Nakamura, M. Kitano, Y. Shirai, T. Ohmi,* Tohoku University, Japan

In a single wafer treatment, an individual process is carried out within 30-40 sec. And an accurate control of the working pressure and composition ratio of all source-gases in the process chamber through the entire process period is essentially required for establishing high quality processes. We have developed a total gas system combining a distribution system and a pumping system in order to satisfy this requirement and the system evaluated using FT-IR method. The gas distribution system consists of an advanced flow controller(FCS) and an electrically controlled valve(ECV). The FCS is introduced into the principal that the flow rate is directly proportional to the upstream pressure when the upstream pressure of a orifice is two times higher than the downstream pressure. The advanced distribution system using the FCS and the ECV does not observe overshoot phenomena and so stable gas flow rate can be distributed in the chamber after valve operation. However, in the case of combination chamber volume and gas flow rate, it occurred time lag to become stable gas concentration in chamber. To solve this problem, we developed the multi-step flow rate control. Consequentially, the working pressure rises momentarily because more gas distributes than steady state gas flow rate. This problem is solved to control the pumping property by changing the purge gas flow rate which supplying into the drug screw pump with the FCS. Combining the advanced gas distribution system using the FCS and the ECV and the pumping system, we can perfectly control process parameters such as gas composition and the working pressure on the moment.

4:00pm **MS-MoA7 Investigating Molecular Contamination in Cleanrooms***, **P.H. Schnabel**, G. Goodman,* Charles Evans & Associates*; D. Nehrkorn, M. Kendall,* Surface Science Laboratories*; G. Strossman, P. Lindley,* Charles Evans & Associates

As the line widths of microelectronic devices approach 0.1 micron, the presence of airborne molecular contamination (AMC) in fabs and cleanrooms has become a major concern for the semiconductor industry. In order to achieve low defect rates in these next generation devices the technical ability to identify, isolate and eliminate AMC is a substantial challenge. AMC can potentially result from every material within a cleanroom or a fab but the main sources for AMC are process chemicals, construction materials and the local environment. AMC defects can cause changes in the wafer's electrical properties, uncontrolled boron or phosphorous doping, etch rate shifts, threshold voltage shifts, wafer and stepper optics hazing and high contact resistance. In this study we demonstrate that TOF-SIMS can be utilized for identifying different types of condensable airborne contaminants and for monitoring those contaminants in cleanrooms. For this purpose witness wafers were placed in a newly constructed class 10 cleanroom and analyzed periodically over a time of 6 months. In order to identify potential sources of AMC the ougassing of individual materials that are typically present in cleanrooms was studied by TOF-SIMS, GCMS and FTIR. The materials under investigation include cleanroom construction materials (e.g. floor tiles, filters, sealant etc.), cleanroom furniture, cleanroom garments and cleanroom utensils. In these experiments each of the materials 'delivers' a fingerprint which can be used to identify potential sources of cleanroom contamination. The transfer of contaminants onto silicon wafers that are brought in contact with these materials was studied as well. The long term objective of this part of our studies is to generate an extensive database which allows us to link the observed contaminants on wafers with potential sources within the cleanroom environment. Both, transfer through the gas phase and by contact will be evaluated.

4:20pm **MS-MoA8 Minimizing Particle Generating Contamination in Polysilicon LPCVD*, J. Krueger,*** Texas Instruments Incorporated*; J. Snow, J. Hardin, J. Gratz,* Millipore Corporation

Increasing wafer size and decreasing critical dimensions exacerbate the chances of a particle coming to rest in a die-killing location. In this study, the effect of point-of-use (POU) purification was evaluated by processing two sets of split lot wafers on an LPCVD polysilicon horizontal furnace. The gas quality downstream of the furnace was evaluated using a closed ion source (CIS) residual gas analyzer (RGA) and an in-situ particle counter (ISPM). Wafer particle counts, film contamination levels by secondary ion mass spectroscopy (SIMS), surface roughness and grain size measurements by atomic force microscopy (AFM) were all used to compare the split lot halves processed with and without purification. SIMS analysis showed that oxygen levels in the film were lower for wafers run with the purifiers. Also, secondary ion counts of silicon were slightly higher in the film of the wafers processed with the purifiers. Wafer particle data showed that wafers run with the purifiers had 72% fewer added defects. The ISPM sensor showed that there were 37% fewer particles with the purifiers in place. RGA results revealed lower moisture levels with the purified silane deposition step compared to unpurified.

4:40pm **MS-MoA9 Highly Concentrated Ozone Gas Supplied at Atmospheric Pressure Condition as a New Oxidizing Reagent for the Formation of SiO@sub 2@ Thin Film on Si*, K. Koike,*** Iwatani International Corporation, Japan*; S. Ichimura, A. Kurokawa, K. Nakamura,* Electrotechnical Laboratory, Japan

Ozone is expected to be one of promising oxidizing reagents for the fabrication of future ULSI device. We have investigated ozone oxidation on Si(100) substrate with high purity (about 80 vol%) ozone gas, and have revealed various merits of ozone oxidation; e.g., ozone can form dense SiO@sub 2@ film on a Si substrate at lower substrate temperature than that used at a conventional thermal oxidation process, ozone can oxidize hydrogen-terminated silicon surface which oxygen molecules cannot, etc.@footnote 1,2@ One major problem which has to be solved before the ozone oxidation is applied to a practical process is low oxidation rate. Since the pressure of the high purity ozone gas was low (typically; <10@super -4@ Pa), only 2 nm thick SiO@sub 2@ film could grow on a Si(100) substrate by 2 hours ozone gas exposure at a substrate temperature of 973K. In the present study, we report that the problem could be solved by fabricating another type of ozone generator. The generator can supply highly concentrated ozone gas at atmospheric pressure condition, by desorbing ozone from silica-gel on which ozone/oxygen mixture gas had been adsorbed at lower temperature. Ozone concentration in the gas from the generator can be changed between 0 and 70 vol%, by controlling the ozone adsorption and desorption condition. Even with 25 vol% ozone gas, it was confirmed that SiO@sub 2@ film as thick as 3.3 nm grew on a Si (100) wafer kept at 648 K by 30 min exposure. The wafer had chemical oxide film (thickness; 1.2 nm) before the ozone oxidation. So SiO@sub 2@ film with thickness of 2.1 nm could be additionally formed with the ozone gas, while under the same experimental condition only 0.6 nm thick SiO@sub 2@ film could be formed on the same wafer with pure oxygen. It should be emphasized that the density of the SiO@sub 2@ film formed with 25 vol% ozone gas was equivalent to the density of a film formed by a thermal oxidation process at 1023K, judging from their etching rates with dilute HF solution. The result suggests that the present ozone oxidation process has high possibility to be adopted as a new process for Si oxidation. The details and performance of the new ozone generator are presented together with the dependence of the oxidation of Si(100) on ozone concentration and on Si substrate temperature. @FootnoteText@ @footnote 1@ A. Kurokawa, S. Ichimura, and D.W. Moon, Mat. Res. Soc. Symp. Proc. 477, 359 (1997). @footnote 2@ A. Kurokawa, K. Nakamura, and S.Ichimura, Mat. Res. Soc. Symp. Proc. 513, 37 (1998).

5:00pm **MS-MoA10 A Comparison of VPD, TXRF, and Surface SIMS to Detect Fe, Ni, Cu, and Al on Silicon Wafers*, V.K.F. Chia,*** *J. Metz, M.J. Edgell,* Charles Evans & Associates

The emphasis on contamination free manufacturing (CFM) continues within the manufacturing environment through the use of cleanrooms and the practice of contamination-free procedures. Stringent contamination limits for polished and epitxial substrates and surface preparation (i.e. before gate oxide growth) are suggested by the National Technology Roadmap for Semiconductors (NTRS). Today's requirement for surface metals is typically in the range of 10@super 10@ at/cm@super 2@. Future needs are anticipated to be in the mid-10@super 9@ at/cm@super 2@. The transition metals Fe, Ni, and Cu are considered to be very damaging at the gate oxide level, and therefore requirements for these are becoming more stringent. Al is important to monitor because at concentrations below 10@super 11@ at/cm@super 2@ it can increase the oxide growth in the very thin gate oxide regime. This is a different effect compared to higher levels of Al (e.g. >10@super 12@ at/cm@super 2@), which decreases gate oxide thickness for thicker gate oxides. VPD, TXRF and SurfaceSIMS are commonly used in surface clean technology. VPD is a collection/scanning procedure that concentrates the metal contaminants on a wafer surface into a droplet. VPD procedure is popular because it improves the detection limit of the final analytical measurement technique. TXRF is well established as a surface sensitive technique. It can detect medium- and high-Z elements (sulfur to uranium) on silicon wafers at very low concentration levels. Routine detection limit is approximately 10@super 10@ at/cm@super 2@ or better. SurfaceSIMS is a powerful analytical technique for substrate engineering. Typical detection limit of this technique is 10@super 8@ to 10@super 10@ at/cm@super 2@. SurfaceSIMS complements TXRF by detecting low-Z elements, such as Li, Na, K, and Al. This presentation provides an overview of VPD, TXRF, and SurfaceSIMS and their application to detect Fe, Ni, Cu, and Al.

Nanometer-scale Science and Technology Division
Room 612 - Session NS1-MoA
Nanoscale Tribology and Adhesion

Moderator: S.S. Perry, University of Houston

2:00pm **NS1-MoA1 Tribological Properties of Self-Assembled Monolayers on Si Surfaces*, J.E. Houston,*** *J.D. Kiely,* Sandia National Laboratories*; J.A. Mulder, X.-Y. Zhu,* University of Minnesota

The use of organic monolayers as lubricating films has recently received considerable attention, especially with regard to their potential use in micromachine applications. We have used the interfacial force microscope (IFM) to characterize, on the nanometer scale, the tribological properties of a new class of self-assembled monolayers on Si(001) surfaces. These films consist of alkyl-OH and NH2 terminated molecules reacted with a fully chlorinated Si surface. We contrast their tribological behavior with those of the more familiar alkylchlorosilane monolayers through measurements of contact hysteresis, lateral frictional force and film conductance as a function of normal load. In addition, we probe the wear behavior under repetitive "wear-track" cycles. The chlorosilane monolayers show high friction coefficients and considerable wear while the films grown on the chlorinated surface show low friction coefficients and little wear, suggesting that the latter has considerable potential as a monolayer lubricant for Si. We discuss these results in terms of what is known concerning the structural and chemical properties of these two types of self-assembled monolayers. This work was supported by the U.S. Department of Energy under contract DE-AC04-94AL85000. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed-Martin Company, for the U.S. Department of Energy.

2:20pm **NS1-MoA2 Contact Hysteresis, Friction and Conductance of Self-Assembled Monolayers on Au*, J.D. Kiely,*** *J.E. Houston,* Sandia National Laboratories

We have investigated the relationship between friction and the mechanical, electrical and chemical properties of self-assembled monolayers of hexadecanethiol on the Au(111) surface using the interfacial force microscope. We find a very low friction coefficient for freshly prepared films with a direct correlation of the frictional force with the contact hysteresis, i.e., the energy dissipated in the film during a loading/unloading cycle. In addition, the film conductance is found to increase exponentially with the applied film stress under loading. Above film stresses of about 4 Gpa, the film compliance and frictional force rise sharply while the conductance remains log linear. To simulate aging in a laboratory environment, we have oxidized films by direct exposure to ozone and find that the frictional force, conductance and hysteresis all rise dramatically. We discuss these results in terms of the known properties of the monolayer films and the findings of previous work on the effects of oxidation by ozone exposure. 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 **NS1-MoA3 Energy Dissipation in Defective Alkanethiol Monolayers*, N.D. Shinn,*** *J.D. Kiely, J.E. Houston,* Sandia National Laboratories

Although highly ordered, alkanethiol self assembled monolayers (SAMs) have a hierarchy of structural defects that lead to dynamic energy dissipation.@footnote 1@ Counter-intuitive friction results on nominally isomorphic monolayers suggest surprising sensitivity to subtle structural differences or demonstrate that extrinsic probe/monolayer interactions dominate friction.@footnote 2@ We separate intrinsic and extrinsic contributions to friction by using a Quartz Crystal Microbalance to inertially shear and simultaneously measure the intrinsic energy dissipation in pure, mixed and damaged alkanethiol SAMs chemisorbed on Au(111)-textured QCM electrodes. For complete monolayers, domain boundaries are the major symmetry-breaking defects that enable dissipation. Point defects created by electron or UV irradiation only incrementally increase the intrinsic dissipation. Residual fluid phases, most notably in sub-monolayer films, lead to the highest dissipative losses. Oxidation by ozone decouples the SAM from the Au(111) substrate and dramatically increases the intrinsic dissipation. Interfacial Force Microscope experiments demonstrate how the structure-dependent SAM viscoelasticity is manifested in controlled friction measurements.@footnote 3@ 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@N. D. Shinn, T. M. Mayer and T. A. Michalske, Tribology Letts. (in press). @footnote 2@ H. I. Kim, T. Koini, T. R. Lee and S. S. Perry, Langmuir 13, 7192 (1997). @footnote 3@J. E. Kiely, N. D. Shinn and J. E. Houston, Langmuir (submitted).

3:00pm **NS1-MoA4 Interaction Forces Measured with Functionalized Cantilevers and SFM Modulation Techniques*, A.L. Szuchmacher*,** *R. Luginbuehl, T. Engel, R.M. Overney,* University of Washington

Understanding local interaction forces between material surfaces is very important for many industrial and research applications such as tribology, materials science, bioengineering, and polymer science. The scanning force microscope allows for measuring forces acting at those interfaces. In order to understand the interactions between probe and material surfaces, the surface chemistry of the SFM tip must be well defined. Ultrasharp silicon cantilevers were reacted with different silanes to produce well defined and covalently bound monolayer films. The quality of these coatings was controlled by different techniques including ESCA and SFM. These tips were used to study the interactions of thin films using force-displacement curves and friction force measurements. Special SFM modulation techniques were applied to probe and image the interfacial interactions. Amplitude and phase response signals will be discussed. Fundamental effects of solvents on van der Waals interactions between surfaces were investigated as well as hydrogen bonding effects. Experiments were carried out as a function of surface chemistry, temperature, solvent, and pH.

3:20pm **NS1-MoA5 SPM Tip-Sample Interactions in Primary Alcohols of Varying Chain Length*, R.M. Ralich*,** *Y. Wu, R.D. Ramsier, P.N. Henriksen,* University of Akron

Interactions between functionalized tips and substrates in scanning probe microscopy (SPM) are usually investigated by utilizing an intervening liquid medium, however the results may be influenced in various ways by the medium itself. In this study the chain length of a series of primary alcohols is shown to affect adhesion measurements. The measurements are performed between a layer of phosphonic acid adsorbed on an aluminum substrate and an aluminum-coated, hydroxyl-terminated silicon nitride tip. These are adsorption systems that have been characterized previously by vibrational spectroscopy and form a stable, well-defined system for studying the effects of the medium on adhesion. Adhesion forces between the tip and sample are observed to decrease as the alcohol chain length is increased. These data imply that a synergistic combination of fundamental interactions is responsible for adhesion in this system.

3:40pm **NS1-MoA6 Sliding Friction of Xenon Monolayers and Bilayers on Pb and Cu Substrates*, S.M. Winder*,** *B. Mason, J. Krim,* North Carolina State University

Studies of the fundamental origins of friction have undergone rapid progress in recent years with the development of new experimental and computational techniques for measuring and simulating friction at atomic length and time scales.@footnote 1@ The increased interest has sparked a variety of discussions and debates concerning the nature of the atomic-scale mechanisms that dominate the dissipative process by which mechanical energy is transformed into heat. We report here our measurements of the sliding friction of xenon monolayers and bilayers sliding on Cu and Pb surfaces. Such studies provide information on the relative contributions of electronic and phononic dissipative contributions to sliding friction, since phonon dissipation is present at all film coverages, while electronic dissipation primarily impacts the monolayer. For the system Xe/Pb the relative contributions of monolayer and bilayer coverages to the measured friction appear similar to those of Xe/Ag(111).@footnote 2@ This indicates the primary mechanism of friction in Xe/Pb and Xe/Ag is through phonons within the adsorbate. The substrate Pb is of particular interest on account of the recent observation of superconductivity-dependent sliding friction on this metal. The system Xe/Cu is interesting because the interaction potential of Xe/Cu is known accurately, allowing highly reliable comparisons of theory to experiment. Work funded by NSF DMR#9896280. @FootnoteText@ @footnote 1@ J. Krim, Scientific American, vol. 275, pp 74-80 (1996). @footnote 2@ C. Daly and J. Krim, Physical Review Letters, vol. 76, pp 803-806 (1996).

4:00pm **NS1-MoA7 Tribological Proprties of Single Crystalline Metal Surface*, A.J. Gellman*,** *J.S. Ko,* Carnegie Mellon University **INVITED**

The tribological properties of single crystal metal surfaces have been measured under the ultra-high vacuum conditions of a surface analysis apparatus. This experiment allows us to measure both friction and adhesion between two single crystal surfaces brought into contact under a wide range of loads, and sheared with a wide range of sliding velocities. Most importantly it is possible to maintain strict control over the chemistry and properties of the surfaces. The experiments performed to date have systematically varied a number of surface characteristics in order to observed their effects on tribological properties. The clean surfaces of singles crystals can be brought together under varying orientation. Experiments with Ni(100) surfaces have shown that the crystallographic orientation can affect the frictional properties of the interface. These result in variations of the friction coefficients over a fivefold range. Furthermore the effects of crystallographic oreintation propagate through adsorbed layer of thickness up to four monolayers. The effects of orientation are thought to result from plastic deformation in the bulk solid of the metal crystals. The effects of adsorbed species can be measured with an extremely high level of control over the nature of the adsorbate, its coverage and its chemistry. On both Cu(111) and Ni(100) surfaces we have observed that at coverages less than one monolayer adsorbed species have little or no influence on interfacial friction. This has been observed using both atomic and molecular adorbates. It is thought that for adsorbed films at coverages less than one monolayer direct metal-metal junctions across the interface cause displacement of adsorbed species from the contact region. The result is a metal-metal interface with high shear strength similar to that formed between clean surfaces. Finally, the friction between single crystal surfaces can be influenced by fine characteristics of the structure of adsorbed layers. Measurements reveal discontinuous breaks in the friction versus adsorbate coverage for both trifluoroethanol on the Cu(111) surface and ethanol on the Ni(100) surface. These discontinuities are attributed to layering of the adsorbate on the surface. The observation of such effects has been made in several laboratories using the surface forces apparatus to measure friction between perfectly flat mica surfaces. It is remarkable to see similar effects occuring between crystalline metallic surfaces that are plastically deformable.

4:40pm **NS1-MoA9 Combined Quartz Crystal Microbalance and Scanning Probe Microscope Studies of Vapor-Deposited Films on Metal Surfaces*, B. Borovsky*,** *M. Abdelmaksoud, J. Krim,* North Carolina State University

Experimental investigations of friction, lubrication and adhesion at nanometer lengthscales have traditionally been performed by employing force microscopy, surface forces apparatus (SFA), or quartz crystal microbalance (QCM) techniques. While collectively these techniques have yielded much useful information, their results have to date never been mutually cross-referenced. In order to achieve such a cross referencing, we have performed two sets of measurements: (1) A QCM study of the system toluene/Ag(111) with and without C@sub 60@ vapor-deposited on the Ag(111) surface, and (2) a joint QCM/SPM study of the systems Ethylene/Pt and Oxygen/Ag. The former system has been studied by means of SFA,@footnote 1@ whereby it was reported that C@sub 60@ at a toluene/mica surface resulted in a significant reduction in friction levels. The latter studies allow direct comparison of SPM and QCM data, as the measurements are carried out in unison. Our studies of toluene/C@sub 60@ have revealed that the decrease in friction reported in Ref. 1 is most likely due to the manner in which the C@sub 60@ layer adheres to the solid substrate. Meanwhile, we have observed that for ethylene and oxygen adsorbed on Ag, a measurable shift in the frequency and amplitude response of the QCM occurs as the STM tip is dragged through the adsorbed layers. Additionally, allowing rubbing to proceed for extended periods within a small scanned region produces a large contrast with the surrounding region in STM images. The experiment is currently being repeated on a Pt substrate in order to search for a tribochemicallytriggered reaction. Work funded by AFOSR F49620-98-1-02-1 and NSF DMR9896280 @FootnoteText@ @footnote 1@ S.E. Campbell, G. Luengo, V.I. Srdanov, F. Wudl and J.I. Israelachvili, Nature, volume 82, p 520 (1996) .

5:00pm **NS1-MoA10 Sliding Transitions and Dissipation in Nanoscale Contacts***, **K.J. Wahl,*** Naval Research Laboratory*; S.A.S. Asif,* University of Florida

In order to investigate tribological processes at the nanometer scale, we need to better understand how model asperity contacts respond to shear and dissipate energy. In our experiments, we investigate the dynamic processes occurring during the transition from static to sliding contact, as well as during the formation and breaking of nanoscale adhesive contacts. Measurements are made using an atomic force microscope operated in shear modulation mode, where the sample position is modulated laterally with amplitudes as small as a few Å. Both amplitude and phase response of the contacts are monitored using a lock-in amplifier. In this work, we expand our technique to incorporate harmonic analysis of the response of the contact to lateral modulation. As a result, we are now able to distinguish between various types of dissipation including friction, microslip and damping. We demonstrate application of this technique to discriminate between static to sliding contacts as well as identify and quantify microslip in nanoscale contacts.

Nanometer-scale Science and Technology Division
Room 6C - Session NS2-MoA

Quantum Dots and Wires

Moderator: M. Weimer, Texas A&M University

2:00pm **NS2-MoA1 High Resolution Optical Spectroscopy and Control of Single GaAs Quantum Dots***, **D. Gammon,*** Naval Research Laboratory **INVITED**

Recently it has become possible to probe individual excitons localized laterally in narrow GaAs quantum wells using high spatial and spectral resolution optical techniques. Discrete, atomic-like spectra with homogeneously-broadened linewidths as narrow as a few tens of micro-eV have been measured. These linewidths are two orders of magnitude narrower than the ensemble linewidth arising from inhomogeneous broadening and an order of magnitude narrower than the narrowest observed in wide quantum well samples. This extraordinary reduction in linewidth can be explained in part by the removal of inhomogeneous broadening accomplished by probing individual localized excitons, and in part by the reduction in homogeneous linewidth in going from 2D to 0D. In fact, the linewidths are in the regime expected for the intrinsic broadening mechanisms of exciton-phonon interactions and radiative emission. In other words the linewidths may be close to their natural linewidths.@footnote 1@ This great reduction in linewidth attained in PL by probing individual QDs has led to a number of new observations including fine structure splittings,@footnote 2@ hyperfine structure splittings @footnote 3@ and the measurement of the nonlinear response of a single quantum dot.@footnote 4@ Using coherent picosecond pulses, coherent control and the generation of superposition states have been demonstrated.@footnote 5@ These examples of advanced spectroscopies on individual excitons are first steps toward what may eventually lead in its maturity to coherent optical control of QDs comparable to what is now possible in atoms. @FootnoteText@ @footnote 1@ D. Gammon, et al., Science 273, 87 (1996). @footnote 2@ D. Gammon, et al., Phys. Rev. Lett. 76, 3005 (1996). @footnote 3@ S.W. Brown, et al., Phys. Rev. B 54, R17339 (1996); D. Gammon, et al., Science 277, 85 (1997). @footnote 4@ N. H. Bonadeo, et al., Phys. Rev. Lett. 81, 2759 (1998). @footnote 5@ N. H. Bonadeo, et al., Science 282, 1473 (1998).

2:40pm **NS2-MoA3 Quantum Dots; The Small World of Artificial Atoms***, **L.P. Kouwenhoven,*** Technical University of Delft, The Netherlands **INVITED**

We performed transport experiments on quantum dots in which the electron number can be tuned from 0 to 1, 2, etc. The addition spectrum shows a shell structure corresponding to a 2D harmonic confinement potential. The magnetic field dependence shows that the single particle states are spin degenerate and filled with two electrons. The filling of a shell occurs according to Hund's rule: electrons occupying degenerate states prefer to have parallel spins which lowers the total energy due to an increased exchange interaction. We observe such Hund's rule states at zero magnetic field and also at level crossings in a finite magnetic fields. In non-linear transport characteristics also the first few excited states are visible which we have studied over a magnetic field range up to 16 Tesla. The magnetic field induces transitions between ground states and excited states and also between excited states. In the high magnetic field regime all electrons are in the lowest orbital Landau level. This is the quantum Hall regime for a small electron system where the electrons form a strongly interacting many-body system. We have observed in the few-electron regime (N<10) so-called singlet-triplet oscillations. On increasing the magnetic field for a fixed electron number, we first observe spin-flips (between the two spin states of the lowest orbital Landau level), then the maximum density droplet (when all electrons are spin polarized and occupy the state with the lowest angular momentum), and then a reconstruction (probably an edge reconstruction, either spin polarized or with a spin texture). @FootnoteText@Work done in collaboration with D. Austing, M. Eto, T. Honda, S. Tarucha, M. Danoesastro, J. Janssen, R. van der Hage, and T. Oosterkamp.

3:20pm **NS2-MoA5 Low-Temperature Tunneling Spectroscopy of the Tip-induced Quantum Dot on n-InAs(110)***, R. Wiesendanger,* ***M. Morgenstern,*** *R. Dombrowski, Ch. Whittneven,* University of Hamburg, Germany

The local tip-induced band bending in scanning tunneling microscopy (STM) studies of semiconductor surfaces leads to a quantum-dot-like potential. Scanning tunneling spectroscopy (STS) on n-InAs(110) at negative sample bias has been applied to determine the energies of the quantized states of the tip-induced quantum dot. Additionally, the magnetic-field dispersion of these states has been studied showing clearly the expected splitting of the first excited state in agreement with Hartree-Fock calculations. At positive sample bias the local tunneling spectra were found to be dominated by the Landau bands of the tip-induced quantum dot. Moreover, spatially-dependent spin splittings of the Landau bands were observed, induced by the spatially varying spin polarization of the tip-induced quantum dot.

3:40pm **NS2-MoA6 Coherently Strained Sn Quantum Dot Formation in Si via Phase Separation***, **K.S. Min**, H.A. Atwater, N.J. Choly,* California Institute of Technology

Diamond cubic @alpha@-Sn is a zero band gap semiconductor and band structure calculations predict a direct and tunable energy gap for Sn-rich Sn@sub x@Si@sub 1-x@ alloy system. One approach for realization of a direct band gap material based on coherently strained Sn-rich Sn@sub x@Si@sub 1-x@/Si system is to synthesize coherently strained Sn-rich quantum dots. For high Sn concentration Sn@sub x@Si@sub 1-x@/Si quantum dot structures, one might potentially take advantage of quantum carrier confinement to further tune the energy gap over a wide range in the infrared frequency range. The biggest difficulty in growing Sn@sub x@Si@sub 1-x@ quantum dots via conventional epitaxial growth techniques, however, is the strong tendency for Sn atoms to segregate to the surface during growth at ordinary Si epitaxy temperatures. We report a novel two-step process for synthesizing coherent Sn-rich quantum dots contained within Si, where the enthalpy of mixing is highly positive. First, an ultrathin homogeneous Sn@sub x@Si@sub 1-x@ metastable solid solution sandwiched between Si is grown by temperature-modulated molecular beam epitaxy. The as-grown epitaxially stabilized ultrathin homogeneous film is then thermally annealed in high vacuum, whereupon the quantum dots precipitate as the ultrathin alloy film phase separates. The quantum dots appear in planar-view transmission electron micrographs as square-shaped with facets along the elastically soft direction. The mean size ranges from 2 nm to 3 nm for annealing temperature between 500°C and 800°C. Cross-sectional high-resolution transmission electron microscopy reveals that the dots are completely coherent with the Si matrix. The early stage of phase separation proceeds via spinodal decomposition, followed by diffusion-limited coarsening in the late stage. The optical properties of the quantum dots will also be presented.

4:00pm **NS2-MoA7 Hybrid Electrochemical/Chemical Routes to Epitaxial, Luminescent, and Size Monodisperse Semiconductor Nanocrystals on Surfaces.***, **R.M. Penner,*** University of California, Irvine

A fundamentally new approach for synthesizing semiconductor nanocrystals - size-selectively - is described in this talk. Cadmium sulfide (CdS) nanocrystallites (NCs) have been synthesized on the atomically smooth graphite basal plane surface using a hybrid electrochemical/chemical (henceforth E/C) method. This method involves the following steps: 1) Electrochemical deposition of cadmium NCs onto an electrode surface, 2) Electrochemical oxidation of cadmium NCs to yield cadmium hydroxide (hexagonal) Cd(OH)@sub 2@ and, 3) Displacement of oxygen (or hydroxide) by sulfide either in the gas phase (via H@sub 2@S at 300 K) or in the liquid phase (using aq. Na@sub 2@S) solution. Electron diffraction is employed to monitor the progress of this synthesis, and the c rystal structures and orientations of the resulting nanocrystals which have mean diameters ranging from 30Å to 150Å. Wurtzite phase CdS nanocrystals generated by the E/C method possess the following characteristics: Single crystallinity, good-to-excellent si ze monod ispersity, epitaxial alignment (with the hexagonal periodicity of the graphite(0001) surface). In addition, E/C deposited particles on graphite exhibit strong room-tempera t ure photoluminescence (PL) spectra in which virtually no trap state emis sion is o bserved, and the energy of the emitted phonons is tunable based on the crystallite diameter. Extraordinarily good size monodispersity is possible for the CdS nanocrystals prepared by this method. One consequence is that the PL emission line widths seen for ensembles of 300,000 CdS nanocrystals can be as narrow as those seen for single CdS nanocrystals (15 meV at 20 K). V.

4:20pm **NS2-MoA8 High-Bias Conductance of Au Nanowires at 4 K***, **A. Sakai**, K. Yuki,* Kyoto University, Japan

We have studied the bias dependence of the quantized conductance of Au nanowires at 4 K. The experiment was carried out on Au relay contacts which were directly immersed in liquid He. A well-defined 1G@sub 0@ peak (G@sub 0@=2e@super 2@/h is the conductance quantum unit) appears in the conductance histogram, as observed in previous work.@footnote 1@ With increasing the bias, the 1G@sub 0@ peak decreases in height, while its position remains unshifted. This behavior of the 1G@sub 0@ peak is just the same as that observed at room temperature.@footnote 2@ The critical bias V@sub c@ at which the 1G@sub 0@ peak disappears is 2.4 V, which is slightly higher than the values at room temperature (1.9 V) and at 77 K (2.2 V). This weak temperature dependence of V@sub c@ implies that the high-bias instability of the 1G@sub 0@ state of Au is not due to Joule heating effects. Our experimental results are rather consistent with the electromigration of contact atoms which predicts linear and moderate increase in V@sub c@ with decreasing temperature. @FootnoteText@ @footnote 1@J. L. Costa-Krämer, N. García, and H. Olin, Phys. Rev. B 55, 19 (1997). @footnote 2@H. Yasuda and A. Sakai, Phys. Rev. B 56, 1069 (1997).

4:40pm **NS2-MoA9 Quantized Conductance of Metal Nanowires: Is It Useful as a New Device?***, **K. Takayanagi**,* Tokyo Institute of Technology, Japan **INVITED**

As the scale of microelectronic engineering continues to shrink, interest has focused on the quantum nature of electron transport through quantum wires and/or carbon nanotubes and electron storage on quantum dots. We report here firstly measurements of the quantized conductance of metal quantum poin contacts (QPC's) prepared with an STM that we can simultanelusly image using ultra-high vacuum (UHV) electron microscope. This STM-UHV electorn microscope technique allows us to directly observe any relationship between the structure and conductance of the QPC's. We observed gold metal QPC's, and found a single chain of gold atoms suspended between the electrodes. We can thus confirmed that the conductance of a single strand of atoms is 2e@super 2@/h, (13k@ohm@)@super -1@ , where 'e' is the electron charge and 'h' is Planck's constant. The QPC's often can form a very long nanowire suspended between the electrodes, which are ideal one-dimensional channel similarly to carbon nanotubes. To verify structures of such long matal wires, we made stable nanowires by electorn beam irradiation onto a very thin gold film. We first obtained high-resolution images of a linear chain which consists of four suspended gold atoms. The gold atoms had anomalous spacing compared with the nearest neighbor distance of the bulk crystal. Second, the nanowire which appears as three or four atom rows the diameter in TEM images have a structure different from the bulk crystal. It is very promising for microelectronic engineering that long gold nanowires have thier own specific structure and, thus, have definit conductances specific to their structures. @FootnoteText@ H.Ohnish, Y.Kondo, and K.Takayanagi, Nature, 395 (1998) 780.

Organic Electronic Materials Topical Conference
Room 616/617 - Session OE+EM+FP-MoA

Transport and Nanostructures in Organic Films

Moderator: E. Umbach, Universität Würzburg, Germany

2:00pm **OE+EM+FP-MoA1 Generation and Transport of Charge Carriers in Conjugated Polymers***, V.I. Arkhipov, **H. Baessler**, S. Barth, C. Im, D. Hertel, B. Schweitzer,* Philipps Universität, Germany **INVITED**

Upon photoexcitation of conjugated polymers, such as ladder-type polyphenylene (LPPP) and substituted PPVs, both geminately bound electron-hole pairs and free charge cariers are generated. Evidence for geminate pair production in LPPP comes from electric field assisted delayed fluorescence. Intrinsic free charge carrier generation occurs via on-chain dissociation of vibrationally hot singlet excitations. Motion of positive charge carriers has been studied involving time of flight experiments. From the hole mobility in a sieres of substituted PPV as a function of temperature and electric field it will be concluded that transport is disorder controlled as it is in molecularly doped polymers. An exception of this rule is hole transport in LPPP. The question of intra versus inter chain transport will briefly be addressed. This work was supported by the Deutsche Forschungsgemeinschaft (Sonderforschungsbereich 383) and the Stiftung Volkswagenwerk.

2:40pm **OE+EM+FP-MoA3 Resistance of Individual Molecular Semiconductor Grains Measured by Conducting Probe Atomic Force Microscopy***, **T.W. Kelley**, C.D. Frisbie,* University of Minnesota

Continued interest in organic electronics has underscored the need for better understanding of transport mechanisms in polycrystalline films of organic semiconductors. We are employing conducting probe atomic force microscopy (CP-AFM) to measure the electrical resistances associated with individual grains and grain boundaries in thin films of @alpha@-sexithiophene (6T). These measurements focus on single 6T grains that are several microns in length and width and 1 - 6 molecular layers (2-14 nm) in thickness. The 6T grains are vacuum deposited onto insulating substrates with lithographically patterned gold electrodes. A Au-coated AFM probe is used to image each grain, including any crystal defects, and to subsequently make point-contact electrical measurements at particular positions on the grain. Current-voltage (I-V) curves are recorded at each position as a function of probe-electrode separation. From these data, we estimate tip-grain contact resistance and conductivity of each grain. In general, we show that CP-AFM is a powerful approach to exploring the effects of microstructure on conductivity in organic semiconductor films.

3:00pm **OE+EM+FP-MoA4 Self-Assembled, Template-Based Nanolithography***, **S.R. Cohen**, R. Maoz, E. Frydman, J. Sagiv,* Weizmann Institute of Science, Israel

The versatility of our recently developed technique@footnote 1@ for scanning probe microscope (SPM)-based, non-destructive nanolithography on an organized organic monolayer template is demonstrated here. By building on, rather than destroying the organic "resist", consisting of an ordered self assembled monolayer (SAM), it is possible to construct complex 3 dimensional structures which can ultimately lead to device formation. In the first step, applying a bias voltage between a conductive SPM tip and a silver thiolate-based monolayer surface site leads to "activation" of that site by the tip. The second step, deposition of metal (silver) from solution by interaction with an enhancing solution which specifically deposits silver on these sites, leads to in-situ formation of metallic features with sub-micron resolution. These features are chemically bound to the surface-altered monolayer, and comprise a three-dimensional structure of surface-bound silver. The fabrication of conducting nanowires is demonstrated, which could be extended to device or nanocircuit formation. The formation of complex, three-dimensional structures with order determined by the underlying monolayer has been demonstrated. Considering that the surface template exhibits molecular order, this technique has the potential of creating molecular-scale devices, using standard ambient application of SPM, and solution chemistry. @FootnoteText@ @footnote 1@ R. Maoz, S.R. Cohen, and J. Sagiv, Adv. Mater. 11, 55 - 61 (1999).

3:20pm **OE+EM+FP-MoA5 Fabrication of Organic Microstructures Using Soft Lithography***, **G. Whitesides**,* Harvard University **INVITED**

Chemistry, with stimulus from biology, is beginning to develop a range of new concepts for fabrication of microsystems: these include self-assembly, non-covalent synthesis, microprinting, micromolding, microfluidic patterning, microelectrochemistry, and related techniques designed to make it possible to design complicated structures having electrical, optical, biological or magnetic functionality and to replicate these systems efficiently. These concepts suggest approaches to fabrication that are substantially different from photolithography in their areas of application. The phrase "soft lithography" encompasses one core set of techniques for replication. The techniques included in soft lithography include the formation of self-assembled monolayers, the patterning of these monolayers using microcontact printing, the fabrication of structures inside small channels using microfluidic methods, and the fabrication of small (< 50 nm) polymer structures using transfer molding and replica molding. The adjective "soft" in the phrase "soft lithography" refers to the elastomeric stamps or molds that are important in many of these techniques, and to the properties of organic materials in general. These techniques may use photolithography, but normally primarily during the step that fabricates the master. This talk will outline progress in this area: from homogeneous self-assembled monolayers (SAMs) to transistors, and from molecular self-assembly to the self-assembly of macro-scale objects. Areas of application in which soft lithography is promising include 3-D fabrication and pattern transfer to non-planar surfaces, large-area patterning, low-cost additive fabrication, rapid prototyping (especially of microanalytical and microfluidic systems), fabrication of systems where control of surface chemistry is crucial (e.g., cell biology) and fabrication of MEMS. Key problems are defect densities, distortions in the elastomeric masks/stamps/molds, and fabrication requiring multiple registered levels of fabrication. Reviews: "Soft Lithography" Xia, Y. and Whitesides, G. M., Angew. Chem. Intern. Ed. Engl. 1998, 37, 550-575. "Soft Lithography" Xia, Y. and Whitesides, G. M., Annu. Rev. Mater. Sci. 1998, 28, 153-184.

4:00pm **OE+EM+FP-MoA7 Electron Beam Patterning of Amine-Functionalized Self-Assembled Monolayers***, **C.K. Harnett**, K.M. Satyalakshmi, M.G. Metzler,* Cornell University*; D.R. Medeiros,* IBM T.J. Watson Research Center*; H.G. Craighead,* Cornell University

Amine-functionalized self-assembled monolayers form a hydrophilic surface that can strongly attach other materials. Examples of materials that have been selectively deposited on patterned amine monolayers include nanoparticles,@footnote 1@ metals, fluorescent molecules, and biological cells.@footnote 2@ Nanopatterning of reactive monolayers is therefore of great practical interest. We have studied electron-beam patterning of 3-aminopropyltriethoxysilane (APTS) and other self-assembled monolayers. Submicron features that are difficult to achieve with UV lithography or microcontact printing are accessible with electron beams. Exposed patterns are examined with lateral-force microscopy (LFM) to determine pattern quality vs. electron dose. At 20 kV, a dose of 300 µC/cm@super 2@ is required to produce continuous 1-micron lines. Results from several electron energies will be presented, with the goal of using these monolayers in a low-energy (1-2 kV) electron-beam lithography system. Exposed areas are analyzed with grazing angle IR spectroscopy to determine possible exposure mechanisms. Subsequent deposition of metals, and use of protection-group chemistry to produce a tone-reversed pattern, will also be discussed. @FootnoteText@ @footnote 1@ T. Vossmeyer, S. Jia, E. Delonno, M. R. Diehl, S.-H. Kim, X. Peng, A. P. Alivisatos, J. R. Heath, Journal of Applied Physics 84, 3664-3670 (1998) @footnote 2@ C. S. Dulcey, J. H. Georger, V. Krauthammer, D. A. Stenger, T. L. Fare, J. M. Calvert, Science 252, 551-554 (1991).

4:20pm **OE+EM+FP-MoA8 Liquid Crystal Imprinting: A New Method for Preparing Uniformly Oriented Thin Films***, **D.L. Patrick,*** Western Washington University

A new synthetic strategy is presented for preparing nanostructured thin films possessing macroscopically-uniform organization. The method is based on the use of a thermotropic nematic liquid crystal (LC) solvent, which serves a growth medium for deposition of material onto a suitable substrate. Application of a magnetic field results in the formation of an oriented film whose directionality can be controlled externally. The method has been used to prepare several organic monolayer systems in which the orientation of the films' molecular constituents is highly controlled. We show that orientational order at the solid-fluid interface originates during film nucleation, and that the alignment mechanism is based on anisotropic anchoring interactions between surface adsorbates and the LC solvent. Details of the relationship between molecular-scale surface structure and bulk LC ordering were studied by combining scanning tunneling microscopy and polarized optical measurements of uniformly oriented cells. LC fluids exhibit anisotropic anchoring interactions with most crystalline surfaces, indicating that the method may be applicable to the synthesis of films and layered materials using a wide range of molecular and supramolecular building blocks.

4:40pm **OE+EM+FP-MoA9 Electro-Patterning of Conjugated Polymer Films on Conducting Surfaces Using the Precursor Polymer Approach***, R.C. Advincula,* University of Alabama at Birmingham, US*; S. Inaoka,* University of Alabama at Birmingham*; **D. Roitman,*** Hewlett-Packard Laboratories

Recently, a novel method of depositing ultrathin films of conjugated polymers on conducting surfaces has been investigated by the UAB and HP groups. We report the formation and patterning of conjugated polymer films by novel electro-deposition of materials on specific sites of substrates and sequences. We have investigated a range of feature sizes using this method with features below micron size. We have also investigated the formation of unique blend film structures, with emphasis on light emitting materials. Previous attempts in using electrodeposition resulted in 'brittle' and defective (pinholes) film surfaces. Our results indicate that the overall optical, mechanical quality and physical integrity of the films are superior compared to previously reported systems.

Plasma Science and Technology Division
Room 609 - Session PS-MoA

Plasma Diagnostics I

Moderator: H.H. Sawin, Massachusetts Institute of Technology

2:00pm **PS-MoA1 Diagnostics for Insight into Fluorocarbon Plasma Chemstry***, **H. Sugai**,* Nagoya University, Japan **INVITED**

Understanding and controlling high-density fluorocarbon plasmas for dielectric etching has been requiring innovative tools for plasma diagnostics. First, I present a novel and simple probe called plasma absorption probe (PAP), which enables one to measure the local electron density even when the probe surface is soiled with processing plasmas.@footnote 1@ The PAP is based on the resonant absorption of surface wave excited in a "cavity" at the probe head. Second, I describe a new technique for measuring electron energy distribution function (EEDF), i.e., RF-biased optical probe (RF-BOP).@footnote 2@ These new tools reveal a clear difference between high-density ICP and surface wave plasma in their EEDFs, radical and ionic compositions. In the latter half of presentation, I focus on plasma wall interactions. Steady-state radical density profiles near the wall suggests that radical production on surfaces often exceeds the production by electron-impact dissociation of parent molecule. To give an insight into the mechanism, the time/space resolved measurement of radical density is made in a source gas puffed out repeatedly. This experiment allows us to separate the gas phase from the surface processes in time space. Another approach of ion-beam surface experiment is challenged: an ion beam of fluorocarbon species is injected to a substrate at the energies from 10 to 200 eV, and the radicals produced on the surface are detected as a function of the ion energy. For example, SiF@sub 2@, CF@sub 2@ and CF with less CF@sub 3@ are observed desorbing from silicon surface bombarded with CF@sub 3@@super +@ ion. The relevant fluorocarbon chemistry will be discussed combining the beam study with the plasma experiment. @FootnoteText@ @footnote 1@H. Kokura, K. Nakamura, I. Ghanashev and H. Sugai, to be published in Jpn. J. Appl. Phys. @footnote 2@H. Toyoda et al., Extended Abstract of Int. Conf. Reactive Plasmas / GEC (Maui, 1998) p.27.

2:40pm **PS-MoA3 Comparison of Actinometric and Diode-laser Absorption Measurements of [CF] and [CF@sub 2@] in an Inductively Coupled Plasma Reactor***, **T.M. Bauer**, A. Inoue, P.-T. Ton-Nu, J.L. Cecchi,* University of New Mexico

CF and CF@sub 2@ radicals have been shown to be significant precursors for selective oxide etching. Consequently, diagnostics that measure concentrations of these radicals are of interest for process development, monitoring, and control. We compare two such diagnostics: actinometry and wavelength-modulated diode laser absorption spectroscopy. Actinometry is a relatively simple technique. However, it relies on excited state species measurements and may suffer from unwanted influence from other plasma parameters. The diode laser is a more complicated technique, but it provides absolute ground state concentrations. To carry out these comparisons, we have made actinometric and diode laser measurements contemporaneously on an ICP reactor over a pressure range of 10 to 30 mTorr and rf power range of 200 to 1000 W. Gas feedstocks included C@sub 2@F@sub 6@, CHF@sub 3@, and CF@sub 4@, each with 10% Ar added as an actinometer. Over these ranges, the CF concentration varied from 8x10@super 12@ to 4x10@super 13@ cm@super -3@, as determined by the diode laser. The CF@sub 2@ concentrations ranged from 5x10@super 13@ to 9x10@super 14@ cm@super -3@. Our results indicate that for CF@sub 2@ concentrations greater than 8x10@super 13@ cm@super -3@, the actinometric measurements are proportional to the absolute concentrations measured with the diode laser system, with the same constant of proportionality for all feedstocks and over the entire operating range. For CF@sub 2@ below 8x10@super 13@ cm@super -3@, we observe some deviation of the actinometric data, possibly due to interference from other features in the spectrum. For CF, we find that actinometric measurements are proportional to the absolute concentrations measured by the diode laser as a function of power, however, the constant of proportionality depends strongly on pressure and to a lesser extent on the feedstock. We believe that this reflects an underlying dependence of the CF actinometric signal on electron temperature.

3:00pm **PS-MoA4 Ion Energy Distribution Functions (IEDFs) in NF@sub3@ based Discharges with Various Diluents***, **H. Hsueh**,* The Pennsylvania State University*; B.S. Felker,* Air Products and Chemicals, Inc.*; R.T. McGrath,* The Pennsylvania State University*; J.G. Langan,* Air Products and Chemicals, Inc.

NF@sub 3@ based discharges are commonly used for cleaning residual SiO@sub 2@ and Si@sub 3@N@sub 4@ films formed on the walls of PECVD chambers. In order to find a balance between fast chamber cleaning and overly aggressive cleaning chemistries, which can lead to premature hardware failure, a fundamental understanding of the physical and chemical characteristics of the discharge is required. For this reason, we have measured the relative concentration of the ionic and neutral species, ion energy distribution functions (IEDFs), and the optical emission spectra (OES) present within capacitively coupled parallel plate discharges operated with NF@sub 3@ diluted with either Ar, He, Ne, or O@sub 2@. For reactor operation at a fixed power density of 1.35 W/cm@super 2@ and various NF@sub 3@ mole fractions, we found that when Ar was used as the diluent, the principal ion present was Ar@super +@ for all pressures investigated (0.5-1.5 Torr) and the IEDFs exhibit the highest average energies for all gas mixtures studied. In contrast, for similar reactor operating conditions using helium dilution, He@super +@ concentration was relatively low, with NF@sub 2@@super +@, F@super +@, F@sub 2@@super +@, and N@sub 2@@super +@ all having larger concentrations and the IEDFs for all species have lower energy peaks. When oxygen is used as the diluent, NO@super +@ is the major dominant positive ion species. The IEDFs are also lowered when oxygen is used. A summary of how changes in pressure and gas mixture affect IEDFs for all of the diluent options mentioned above will be presented. Optical emission spectra were also recorded as a reference for all of the discharge conditions investigated.

3:20pm **PS-MoA5 Optical Emission Thermometry Applied to the Measurement of Neutral Gas Temperature within a High-density, Inductively-coupled Plasma Abatement Device***, D.B. Graves, **E.J. Tonnis**, M.W. Kiehlbauch,* University of California, Berkeley

Flowing plasma reactors have proven important as downstream sources of reactive species and show promise for applications such as abatement of perfluorocompounds and other environmentally harmful effluents produced by the semiconductor industry. Recent spectroscopic measurements and simulation predictions in a inductively-coupled plasma source indicate that at high input powers, the neutral gas temperature within the plasma zone can be many times higher than ambient (> 1500 K) depending upon the plasma chemistry. High neutral-gas temperature could alter the dominant chemical mechanisms in the plasma and it is therefore important to measure and compare these results to model predictions. In this work, the neutral temperature of flowing CF@sub 4@/O@sub 2@, C@sub 2@F@sub 6@/O@sub 2@, and CF@sub 4@/H@sub 2@O plasmas was measured at varying input conditions using optical emission thermometry techniques. It was found that the rotational temperature, which was assumed to thermalize with translational temperature, is sensitive to the chemical nature of the plasma. In particular, C@sub 2@-derived (516.5 nm) emission temperatures measured within a CF@sub 4@/O@sub 2@ plasma were estimated at greater than 2000 K, which is several times higher than N@sub 2@-derived (399.8 nm) temperatures (~500 K) observed within a pure N@sub 2@ discharge over the same range of pressures and powers. In addition, the rotational temperatures were found to be relatively insensitive to the input power as long as a high-density discharge was sustained.

3:40pm **PS-MoA6 Using Optical Emission Spectroscopy (OES) to Monitor Different Parameters for a Contact Hole Etch Process between Wet Clean***, **D. Knobloch**,* Infineon Technologies Dresden GmbH & Co. OHG, Germany*; F.H. Bell,* Infineon Technologies AG, Munich, Germany*; J. Zimpel, K. Voigtlaender,* Fraunhofer Institute, Germany

Oxide etch processes in IC-fabrication is gaining more and more importance, since the open area of contact hole processes still decreases and metal etch processes become partly replaced by the dual damascene technology. However, process development and stability issues in a manufacturing environment is still handled by trying to adapt a well known base line process on new applications. A typical example is the use of design of experiments in order to determine the robustness of the process window. We established a plasma monitor module for oxide etch processes to simplify process development, characterize process drifts, investigate process mix, and optimize endpoint detection. The monitor module is based on an optical multi-channel analyzer system that allows simultaneous detection of wavelength ranges between 200-950 nm. The system can be coupled to etch tools via the host net to collect data on a run to run basis. Intelligent data analyses software, such as principa! l component analysis (PCA) and partial least square (PLS) algorithms, is implemented to extract process and equipment relevant parameters. A typical manufacturing issue is the mean time between clean (MTBC) of oxide etch equipment. In general, wet cleans are conducted in case particles or the etch rate non-uniformity exceed certain specifications. Indeed, for the etch chamber under investigation, the decrease of the oxide etch rate at the wafer edge determines the wet clean cycle. We analyzed oxide and silicon surfaces after etching as a function of rf-hours and on different spots of the sample using x-ray photoelectron spectroscopy (XPS). The results show that the etch rate non-uniformity can be correlated to the polymer composition. Moreover, the optical emission data show that analysis of suitable wavelength ranges can be used for physical interpretation of the non-uniformity phenomenon. Furthermore, the influence of process mix on the cleanliness of the etch chamber will be discussed.

4:00pm **PS-MoA7 Radical Detection using Appearance Potential Mass Spectrometry***, **H. Singh**, J.W. Coburn, D.B. Graves,* University of California, Berkeley

Appearance potential mass spectrometry (APMS) has recently gained importance for quantitative measurements of reactive radical species in plasmas. We have characterized the contributions to the APMS signal from the line-of-sight "beam" component and the background component of the species in the ionizer of the mass spectrometer. The beam signal is proportional to the number density of the species in the plasma, while the background component of the signal depends on various factors like the vacuum system design and pump speeds. Single stage differential pumping of the mass spectrometer is generally inadequate as the background signal usually dominates the beam signal for both radical and stable species. This necessitates implementation of modulated beam mass spectrometry using a mechanical chopper in the beam path. With one stage of differential pumping, the uncertainty in the beam component measurements is found to be as large as ±180 %. High beam to background signal ratio (>1.0) is achieved using three stages of differential pumping, and this vastly reduces the uncertainty in the beam component measurement to less than ±10 %. Another source of error in the APMS measurements is due to the lower extraction efficiency of the hot fragment ions produced by dissociative ionization in the ionizer of the mass spectrometer. The collection efficiency of the hot fragments is found to be up to 15 times smaller than that of products of direct ionization. The use of the dissociative ionization signal under plasma-off conditions to calibrate the radical direct ionization signal thus leads to overestimation of the radical number density, and we recommend an argon reference signal to avoid the discrimination effects due to dissociative ionization. The combination of multiple stages of differential pumping, background subtraction, and use of a direct ionization reference signal allows accurate quantitative measurements of radical density at the beam sampling point using APMS.

4:20pm **PS-MoA8 C@sub 4@F@sub 8@ Dissociation Rate Control for Oxide Etch Process Plasma by Changing EEDF***, **S. Noda**, T. Tatsumi, N. Ozawa, K. Adachi, M. Okigawa, M. Sekine,* Association of Super-Advanced Electronics Technologies (ASET), Japan

In a dry etching process of SiO@sub 2@, optimizing the fluxes of chemical species and ion energy is essential to achieve high etch performances. The dissociation rate of reactive gas is one of the important parameters that can be used to control the density of the chemical species, i.e. radicals and ions, and their composition in the gas phase. In Ar based C@sub 4@F@sub 8@plasma in a dual frequency parallel plate reactor system,we showed that the radical density ([CFx]) and the composition ([F]/[CFx]) were well correlated with a relation "@tau@ n@sub e@ <@sigma@v>" (@tau@: gas residence time, n@sub e@: electron density, and <@sigma@v>: dissociation rate coefficient (a function of electron impact dissociation cross section and electron energy distribution function (EEDF)).@footnote 1@ The dissociation rate could be easily controlled by choosing a gas flow rate (@tau@) and a source rf power (n@sub e@) at a constant <@sigma@v> value. For further control, we need to know the effects of the <@sigma@v> which is varied by the EEDF depending on discharge conditions and types of plasma sources. We investigated if the control of dissociation rate and radical density in the gas phase would be possible by changing the EEDF. We employed a C@sub4@F@sub 8@ gas dilution with Xe gas that has a lower ionization threshold energy than Ar. The EEDF profile was determined by the relative intensity method using optical emission spectroscopy (OES).@super 2@ In the Xe based plasma, the EEDF profile was much different from that in the Ar based plasma. The density of high energy-electron (>10 eV) was about ten times lower than that of Ar based plasma at the same n@sub e@ (4 x 10@super 11@ cm@super -3@) and@tau@ (6 msec). It was also confirmed that the dissociation rate of both plasmas were followed by the relation "@tau@ n@sub e@ <@sigma@v>". We conclude that the dissociation rate of reactant gas can be controlled by EEDF and the EEDF monitor may be a preferable way to control the radical composition in CF plasmas. This work was supported by NEDO. @FootnoteText@@footnote 1@T.Tatsumi et al., Jpn. J. Appl. Phys., 37 (1998) 2394. @footnote 2@S.Noda et al., Proc. 20th Symp. on Dry Process, Tokyo (1998) p.235

4:40pm **PS-MoA9 Plasma and Surface Diagnostics in Cl@sub 2@/O@sub 2@ Discharges in Transformer Coupled Plasma Reactors*, E. Edelberg,*** Lam Research Corporation*; S. Ullal, A. Godfrey,* University of California, Santa Barbara*; V. Vahedi, J.E. Daugherty, N. Benjamin, A. Perry, D. Cooperberg, R. Gottscho,* Lam Research Corporation*; E.S. Aydil,* University of California, Santa Barbara

Plasma etching with high density transformer coupled plasma (TCP) reactors has become a ubiquitous process in microelectronics because of its ability to transfer patterns from a mask onto an underlying film with precision unequaled by any of the other etching methods. TCP reactors are operated at low pressures where the mean free paths of species are comparable to reactor dimensions. Thus, the role of walls and surface reactions has increased over the role of gas phase reactions in determining the plasma properties and etching behavior. This is most apparent when a stack of thin films of different materials must be etched sequentially in the same reactor using different gases. Chemicals used for etching one material adsorb onto the walls and contaminate the plasma in the following steps and may have deleterious effects on etching of other materials in the stack. In this study, we have explored the effects of wall adsorbates on the plasma properties. The objective is to understand how chemicals adsorbed on walls during one etching step affect the plasma properties in the following steps. Silicon trench isolation using Cl@sub 2@/O@sub 2@ plasmas is taken as a model process and plasma properties and their dependence on the wall conditions were studied through multiple plasma and surface diagnostics including, downstream Fourier transform infrared spectroscopy, in situ multiple total internal reflection Fourier transform infrared spectroscopy, optical emission actinometry, and Langmuir probe.

5:00pm **PS-MoA10 Oxide Etch Studies in an Inductively Coupled GEC Reference Cell C@sub 2@F@sub 6@ Discharge using Diode Laser Spectroscopy*, W.L. Perry,*** *H.M. Anderson,* University of New Mexico

An inductively coupled GEC Reference Cell has been modified to allow etching of patterned oxide wafers under conditions typical of commercial high density plasma reactors. This study reports on the oxide and photoresist characteristics of the tool as a function of reactor source power, bias power, pressure and heated silicon ring temperature. Diode laser absorption spectroscopy (DLAS), optical emission spectroscopy (OES) and Langmuir probe measurements were made at the same time. These measurements are used to construct response surface models of the tool's plasma chemistry behavior versus oxide and photoresist etch rate behavior. The oxide and photoresist etch rate behavior was found to also be profoundly influenced by the temperature of the cooling wafer chuck, so this became a fifth variable in the study. In a C@sub 2@F@sub 6@ discharge, CF and CF@sub 2@ radical concentrations measured by DLAS were also found to be highly dependent on wafer chuck temperature. In a 6 mTorr C@sub 2@F@sub 6@ discharge at 350 W source power and 75 W bias power, typical CF and CF@sub 2@ concentrations were in the range of 1x10@super12@ cm@super -3@ and 3x10@super 13@ cm@super -3@ range. However, if the wafer temperature is allowed to rise toward 100 C, the CF@sub 2@ concentration increases dramatically apparently due to greater photoresist interaction with the plasma. If the wafer is properly cooled, the oxide and photoresist etch rates appear to be dominated by bias power and at low bias power, net deposition of fluorocarbon polymer prevails over net etching. However, with increased wafer temperature, both power and bias exert a strong influence on film etch rates and etching occurs at even zero applied bias power. The data is expected to provide an important database for models of oxide etching in inductively coupled plasma tools. This project was funded by SEMATECH.

Surface Science Division
Room 606 - Session SS1+EM-MoA

Metals on Oxides

Moderator: U. Diebold, Tulane University

2:00pm **SS1+EM-MoA1 Nucleation and Growth of Copper Islands on TiO@sub2@(110): Evidence for Self-limited Island Sizes*, D.A. Chen,*** University of South Carolina*; M.C. Bartelt, R.Q. Hwang, K.F. McCarty,* Sandia National Laboratories

Metal-oxide interfaces play an important role in a variety of technological applications, including those involving the design of electronic devices, sensors and heterogeneous catalysts. In order to develop a fundamental understanding of these metal-oxide interfaces, we have studied the formation of Cu islands on TiO@sub2@(110)-(1x1) in ultrahigh vacuum using scanning tunneling microscopy for Cu coverages up to 1.25 ML. The formation of 3D islands at all the coverages reflects the relatively high mobility of Cu atoms on TiO@sub2@ at room temperature and the weak interactions between Cu and TiO@sub2@. Surprisingly, the island diameter remains almost constant for all coverages. Furthermore, the Cu islands exhibit self-limiting growth at low coverages (0.5 ML), the average island size scales with coverage, but this increase in island size is primarily due to an increase in height not diameter. Although larger islands can be formed by annealing, the average size of the islands is independent of coverage for any given annealing temperature. We propose two general schemes that could lead to the observed self-limiting growth. The first is that the attachment rate of adatoms drops as the island size increases. The second is that the rate at which adatoms reach existing islands drops as the islands grow. We will discuss physical scenarios under which each of these effects may be dominant. This work was performed under the U.S. Department of Energy contract DE-AC04-94AL85000 and supported in part by the USDOE-OBES-Division of Materials Sciences.

2:20pm **SS1+EM-MoA2 Influence of Surface Reactions on Morphology: Ag Nanoclusters on TiO@sub 2@(110)*, X. Lai,*** *T.P. St. Clair, D.W. Goodman,* Texas A&M University

The effects of in situ O@sub 2@ exposure on TiO@sub 2@(110)-supported Ag nanoclusters were investigated using x-ray photoelectron spectroscopy (XPS) and scanning tunneling microscopy (STM). An oxygen-induced cluster ripening was observed by STM after exposing Ag/TiO@sub 2@(110) to 10.00 Torr O@sub 2@ in an elevated-pressure reactor. A bimodal size distribution of Ag clusters was evident after a 10 minute O@sub 2@ exposure at room temperature. Time-dependent studies of the ripening process indicated that the majority of the ripening occurred within the first hour of exposure. The cluster density also increased 5-15%, indicating that redispersion simultaneously occurred with ripening. For comparison, a reduced, roughened TiO@sub 2@(110) and a fully oxidized TiO@sub 2@(110) were prepared and used as Ag supports. Propylene exposure was also studied to further investigate adsorbate-induced morphological changes. Issues relevant to the stability of Ag catalysts for general oxidation reactions were addressed.

2:40pm **SS1+EM-MoA3 Kinetics and Dynamics of Substrate and Metal Atoms on TiO@sub2@*, G. Thornton*,** *I. Brookes, H. Raza, C.L. Pang, S. Haycock,* Manchester University, UK **INVITED**

TiO@sub2@ substrates have been used as platforms to test ideas about oxide surface reconstruction and metal growth on oxides. This work is motivated by the importance of such interfaces in a number of applications which include catalysis and gas-sensing. As part of this work we have recently studied two aspects of TiO@sub2@ surface science associated with temperature and time dependent structural changes using STM and non-contact AFM. The first involves the study of the 1x1 to 1x3 phase transition of TiO@sub2@(100). In addition to the 1x1 and the high temperature equilibrium 1x3 microfacet termination previously observed, intermediate 1x3 structures are imaged. The relationship between the 1x1 termination and the 1x3 microfacet phase suggests that the latter reconstruction is formed by removing material rather than growing from a lower lying terrace. Intermediate structures point to a mechanism of the phase transition which involves discrete bond breaking steps. Turning to Cu growth on TiO@sub2@(110), at room temperature and at <0.1 ML most of the metal atoms are initially mobile, with some 2D island formation. The cluster size of about 6 Å diameter suggests that they consist of 7 atoms arranged in a centred hexagon. Such an arrangement fits between the bridging O rows. 3D clusters are formed at higher coverage consistent with Volmer-Weber growth. At lower temperatures 1D metastable strings of Cu atoms are formed in the [001] direction, which collapse to 2D islands and subsequently 3D clusters at higher coverage.

3:20pm **SS1+EM-MoA5 Nucleation and Growth of Pt Nanoclusters on TiO@sub 2@ Rutile and Anstase Surfaces**, ***Y. Liang,*** Pacific Northwest National Laboratory*; A.W. Grant,* University of Washington*; D.R. Baer, S. Gan,* Pacific Northwest National Laboratory

Understanding the interaction of ultra-thin metal overlayers with oxide surfaces impacts a wide range of technological applications. One of those is the oxide-supported metal catalysts where unusual surface chemisorption and activity have been observed. In this presentation, we report an investigation of nucleation and growth of Pt on rutile and anatase surfaces using scanning tunneling microscopy, x-ray photoelectron spectroscopy, and low energy electron diffraction. Results show that vapor deposition of 0.1 ML of Pt on a rutile TiO@sub 2@(110) surface at ambient temperature leads to the formation of randomly distributed three-dimensional Pt nanoclusters on the 1x1 surface. However, this random distribution is strongly perturbed by the presence of surface line defects produced by extended sputtering and annealing cycles. As the density of the line defect increases, majority of Pt nanoclusters are preferentially attached at the ends of line defects instead of randomly distributed on the rutile surfaces. This result suggests that the line defects on TiO@sub 2@(110) surfaces have stronger interaction with Pt and thus serve as nucleation sites for Pt growth. Based on the change of distribution of Pt clusters as a function of line defect density, the diffusion length of Pt on rutile surfaces is obtained. In addition to rutile, we also investigate the nucleation and growth of Pt on anatase surface. We have successfully grown anatase single crystal thin films on SrTiO@sub 3@ substrates using oxygen plasma assisted molecular beam epitaxy. Investigation of nucleation and growth of Pt on anatase surface is currently in progress. The results will be presented at the meeting and compared with those obtained on the rutile TiO@sub 2@ surfaces.

3:40pm **SS1+EM-MoA6 Role of Surface Vacancies and Water Products in Metal Nucleation: Pt/MgO(100)**, *A. Bogicevic,* ***D.R. Jennison,*** Sandia National Laboratories

Metal atom adsorption on oxide surfaces, resulting in clusters or thin films, involves a variety of structure-determining chemical interactions. While surface steps have long been known to promote nucleation, it has been speculated in several experimental studies that the most common defect in well prepared surfaces, isolated surface oxygen vacancies, may act as nucleation sites. However, this has not been substantiated via experiment or theory. Here we examine this question and, for completeness, how water dissociation products affect nucleation, since there have been several reports that these are common low-density contaminants on prepared oxide surfaces. Our density-functional calculations reveal that isolated F@sub s@ and V@sub s@ surface vacancies on MgO(100) ionize single Pt atoms, roughly tripling their adsorption energy. This trapping inhibits Pt atoms from binding to other Pt atoms, resulting in a negative addimer binding energy. Hence, isolated surface vacancies demote nucleation, contrary to popular belief. A defect that does promote nucleation is the F@sub s@V@sub s@ divacancy, which increases the addimer binding energy by 20%. Amongst water and its dissociation products, adsorbed hydroxyl ions are found to have a similar but even stronger effect. We discuss the implications of these results for the temperature dependence of nucleation and the generality of these results for other metals and oxides.@footnote 1@ @FootnoteText@ @footnote 1@ Sandia is operated by Sandia Corporation, a Lockheed Martin Company, for the US DOE under Contract DE-AC04-94AL85000.

4:00pm **SS1+EM-MoA7 Metal Particles on Single Crystal Oxides as Model Catalysts**, ***J.H. Larsen,*** *J.T. Ranney, A.W. Grant, D.E. Starr, J.E. Musgrove, C.T. Campbell,* University of Washington

The growth morphology and reactivity of model oxide-supported metal catalysts are intimately connected. On some well-defined oxides, vapor-deposited metals form two-dimensional islands, typically up to a critical coverage below 1 monolayer (ML). The local electronic environment of the supported metal particles is modified as compared to the surface of the bulk metal, and so changes in reactivity are expected. Above the critical coverage, three-dimensional growth sets in and it becomes possible to measure reactivities as a function of island thickness. Several metal on metal oxide systems were studied. The surface growth mode was investigated using low energy ion scattering (LEIS) and x-ray photoelectron spectroscopy (XPS). In order to probe the nature of the reaction sites on the surface, the decomposition of hydrocarbons was also studied with temperature programmed desorption (TPD). From these experiments, the dependence of the metal reactivity on the lateral dimensions of the two-dimensional metal islands and the thickness of three-dimensional metal clusters was determined. It was found that Pt particles on ZnO(0001)-Zn exhibit reactivity towards methanol decomposition which is characteristic of low-index Pt facets, even below the critical coverage of ~ 0.6 ML where only two-dimensional islands are present. The adsorption energy of some metal on metal oxide systems was furthermore measured as a function of coverage using single crystal adsorption calorimetry. The adsorption energy is a fundamental quantity that gives important insight into the energetic origins of the growth and reactivity of metal particles supported on metal oxides.

4:20pm **SS1+EM-MoA8 High-Pressure STM Studies of Pt Nano-clusters on Al@sub 2@O@sub 3@/NiAl(110)**, ***L. Österlund,*** *M.O. Pedersen, P. Thostrup, K.H. Hansen, E. Laegsgaard, I. Stensgaard, F. Besenbacher,* University of Aarhus, Denmark

A novel system in which an STM is incorporated into a high pressure cell has been constructed. The system permits in-situ studies of surfaces with atomic resolution at pressures ranging from UHV to one atmosphere. In the present paper, we have investigated the morphology and structure of well-ordered Pt nano-clusters deposited on thin layers of aluminum oxide created by oxidation of NiAl(110). >From the shape, i.e. the height and width, and from atomic resolved images of the top facets of the clusters, we can quantitatively determine the adhesion energy of the metal cluster to the oxide, using calculated surface free energies for the cluster facets. We have investigated the change in the morphology of the Pt nano-clusters exposed to up to 1 bar of hydrogen and oxygen.

4:40pm **SS1+EM-MoA9 Cu Interaction with Al@sub 2@O@sub 3@ Substrates: Effects of Defects and Coverage**, *C. Niu, K. Shepherd,* ***J.A. Kelber,*** University of North Texas

We report UHV surface science studies of the wetting and nucleation behavior of Cu on sapphire(0001). Such fundamental wetting and nucleation interactions are of increasing importance in microelectronics, joining and brazing, as well as in catalysis. This study focuses on the effects of defects and kinetic factors for well-defined systems that are critical to an understanding of behavior for "real world" systems. On clean sapphire, Cu is initially present as Cu(I) to a coverage of 0.35 ML [ML = monolayer], after which a second, metallic Cu layer begins to grow. This behavior is in agreement with recent theoretical calculations by A. Bogicevic and D. R. Jennison[Phys. Rev. B (in press)]. The behavior of Cu on sapphire at elevated temperatures is coverage dependent. For @theta@@sub Cu@ < 0.35 ML, Cu(I) remains stable on the surface for temperatures up to ~ 1000K. However, in the presence of Cu(0), e.g. @theta@@sub Cu@ = 0.75 ML, Cu(I) reacts to form additional Cu(0) at about 500K. Pre-sputtering of the sapphire surface prior to Cu deposition inhibits Cu(I) formation and enhances Cu(0) formation at low coverage, correlating with the sputter-induced dehydroxylation of the sapphire surface and creation of oxygen vacancies. These data indicate that variations of a small number of surface defect densities can explain the large number of contradictory results obtained for the Cu/alumina systems. The significance of these findings to "real world" applications (e.g. Cu on oxidized Ta and other microelectronics diffusion barriers) will be discussed.

5:00pm **SS1+EM-MoA10 Nucleation and Growth of Tungsten on SiO@sub 2@ During Atomic Layer Deposition Using Sequential Surface Reactions**, ***J.W. Elam,*** *C.E. Nelson, R.K. Grubbs, S.M. George,* University of Colorado, Boulder

The atomic layer deposition of tungsten (W) can be achieved by separating the binary reaction WF@sub 6@ + Si@sub 2@H@sub 6@ --> W + 2SiHF@sub 3@+ 2H@sub 2@ into two half-reactions. Successive application of the WF@sub 6@ and Si@sub 2@H@sub 6@ half-reactions in an ABAB... sequence produces W atomic layer controlled growth. The nucleation and growth of W on SiO@sub 2@ was examined during alternating exposures to Si@sub 2@H@sub 6@ and WF@sub 6@. Auger electron spectroscopy studies at 573 K revealed an initial nucleation phase that was followed by a layer-by-layer W growth regime. Nucleation occurred during the first 10 sequential Si@sub 2@H@sub 6@ and WF@sub 6@ surface reactions. Layer-by-layer W deposition then proceeded at a growth rate of 2.5 Å per AB reaction cycle. This W growth rate is consistent with one W monolayer per AB reaction cycle. The Auger data was fit well assuming Frank-van der Merwe layer-by-layer growth. These studies reveal that the sequential surface reactions can facilitate metal wetting of oxide surfaces and conformal layer-by-layer metal growth. Additional Auger experiments yielded the adsorption kinetics for both Si@sub 2@H@sub 6@ and WF@sub 6@ during W atomic layer deposition. The WF@sub 6@

half-reaction had an activation energy E=7 kcal/mol and required WF@sub 6@ exposures of 30 L for the WF@sub 6@ half-reaction to reach completion. The Si@sub 2@H@sub 6@ had virtually no temperature dependence and the Si@sub 2@H@sub 6@ half-reaction saturated following 200 L Si@sub 2@H@sub 6@ exposures at 573 K.

Surface Science Division
Room 607 - Session SS2-MoA
Reactions on Metals

Moderator: F. Zaera, University of California, Riverside

2:00pm **SS2-MoA1 Surface Chemistry on Stepped Pt Surfaces - What Happens at the Steps?***, **J.T. Yates, Jr.**, C.E. Tripa, T.S. Zubkov,* University of Pittsburgh*; M. Mavrikakis, J.K. Norskov,* Technical University of Denmark, Denmark **INVITED**

H.S. Taylor postulated in 1925 that step sites on metallic surfaces are active sites for catalytic reactions. This postulate has become one focus of surface science research since the 1970's. We have studied both photochemical processes and thermally driven processes which occur specifically at metallic step sites. The photodecomposition of adsorbed O@sub 2@ on Pt(335) and Pt(779) surfaces has been used to study the reaction of photogenerated O atoms with CO molecules on both step and terrace sites producing CO@sub 2@. A surface-aligned photochemical process is observed. In addition, the chemisorption of N@sub 2@ on the step sites of these two crystals has been investigated by infrared spectroscopy and by kinetic methods. Linear arrays of weakly-based N@sub 2@ molecules have been observed and their properties will be described. N@sub 2@ does not adsorb on the (111) terrace sites separating the steps.

2:40pm **SS2-MoA3 Investigations of the Role of Edges on the Reaction Kinetics on Nanometer-sized Catalyst Particles using Monte Carlo Simulations***, **H. Persson**, P. Thormahlen,* Chalmers University, Sweden*; V.P. Zhdanov,* Boreskov Institute of Catalysis, Russia, Sweden*; B. Kasemo,* Chalmers University, Sweden

From basic research on single crystals of catalytic materials, it is today well established that the rate of a catalytic reaction may vary considerably from one crystal face to another@footnote 1@ and that defect sites such as steps, kinks, surface vacancies, adatoms etc, may have different catalytic activities than the perfect terrace sites.@footnote 2@ In addition, there are (for supported catalysts) additional types of sites located at the particle-support boundary. It is therefore not surprising that a wide variety of behaviours of catalytic activity versus particle size have been observed,@footnote 3@ sometimes differing considerably from single crystals. The collective set of such differences and the challenge to understand and explain them is referred to as the "structure gap" in catalysis. This presentation will be focussed on Monte Carlo simulations of the kinetics of supported nm catalyst particles, being large enough to have attained bulk-electronic properties.@footnote 4,5,6,7@ The basic underlying mechanisms for the phenomena we will analyse are: (i) the different catalytic activities on different facets of a small supported crystalline particle become coupled in a strongly non-linear fashion due to diffusion occuring over facet boundaries, (ii) different kinetic rate constants at the facet boundaries of a supported particle compared to those for the perfect facets give rise to new kinetics, (iii) and spillover by diffusion of reactants, between the particle and its support, also create new kinetics. The main focus will be on how edges may affect the reaction kinetics. @FootnoteText@ @footnote 1@ R. Imbihl and G. Ertl, Chem. Rev. 95 (1995) 697. @footnote 2@ J.T. Yates, J. Vac. Sci. Technol. A 13 (1995) 1359. @footnote 3@ P.L.J. Gunter et al Catal. Rev. Sci. Eng. 39 (1997)77 @footnote 4@ V.P. Zhdanov, B. Kasemo, Surf. Sci. 405 (1998) 27. @footnote 5@ V.P. Zhdanov, B. Kasemo, Phys. Rev. Lett. 81 (1998) 2482. @footnote 6@ H. Persson et al., J. Vac. Sci. Techn. A (1999), in press. @footnote 7@ H. Persson et al, Catal. Today (1999), in press.

3:00pm **SS2-MoA4 Dissociation and Desorption of NO and N@sub 2@ on Rh(100) and Rh(111), Effect of Surface Structure on Elementary Reaction Steps***, **M.J.P. Hopstaken**, J.W. Niemantsverdriet,* Eindhoven University of Technology, The Netherlands

Removal of NO@sub x@ is an important issue in automotive exhaust catalysis. On the molecular level, dissociation of NO on rhodium is the crucial step in the reduction of NO by CO, H@sub 2@ or hydrocarbons. Here we use TPD/SIMS to study reactions of NO on Rh(100) and compare with similar results on Rh(111).@footnote 1@ On both surfaces the reaction rates of the different elementary steps depend highly on coverage. At low coverage, dissociation of NO is completed around 250 K and 340 K for the Rh(100) and the Rh(111) surface, respectively. When the surface is saturated with NO, dissociation only starts when NO desorbs i.e. when empty sites become available. However, inhibition of NO dissociation at higher coverages cannot be explained by site blocking alone. Monte Carlo simulations strongly indicate that the activation energy for dissociation of NO on Rh(111) increases when other adsorbates such as N, O, and NO are present. At low coverages we find an activation energy of 45 kJ/mole for dissociation of NO on Rh(100), which is 20 kJ/mole lower than on Rh(111). Desorption of NO from both surfaces proceeds at similar rates. However, formation of N@sub 2@ is slower on Rh(100). Apparently, bond breaking of NO is faster and formation of a N-N bond is slower on the more open Rh(100) surface. This can be explained on the basis of surface chemical reactivity theories.@footnote 2@ Unexpectedly, the oxidation of CO to CO@sub 2@ proceeds much faster on Rh(100) than on Rh(111). This, together with the higher rate of dissociation and lower rate of N@sub 2@ formation, has important consequences for the kinetics of the CO + NO reaction on the different rhodium surfaces. @FootnoteText@ @footnote 1@ H.J. Borg, J.P.C.-J.M. Reijerse, R.A. van Santen and J.W. Niemantsverdriet, J. Phys. Chem. 101 (1994) 10052. @footnote 2@ R.A. van Santen, J.W. Niemantsverdriet, Chemical Kinetics and Catalysis, Plenum Press, New York, 1995.

3:20pm **SS2-MoA5 Interactions between CO and NO on Rh Loaded Ceria Films***, **D.R. Mullins**, Lj. Kundakovic, S.H. Overbury,* Oak Ridge National Laboratory

CO and NO were adsorbed sequentially on model catalysts composed of submonolayer amounts of Rh deposited on highly crystalline thin films of reduced cerium oxide. The chemical state of the adsorbed species was monitored by soft x-ray photoelectron spectroscopy (SXPS). It has previously been shown that a reduced ceria substrate promotes the dissociation of CO and NO on supported Rh, with essentially full dissociation occurring by 400 K or 500 K for adsorbed NO and CO, respectively. At a constant temperature of 200 K, a saturation coverage of CO blocks subsequent adsorption of NO, and vice versa. However, the reaction of CO or NO with the dissociation products of the other molecule leads to new states in the C 1s and N 1s SXPS spectra that do not occur if either gas is adsorbed separately. If NO is dosed first and then heated to decompose it into atomic N and O, subsequent CO exposure at 200 K leads to new high binding energy states in the C1s and O 1s spectra which appear after annealing to 400 K. The binding energies of these states are consistent with formation of CO@sub 2@ on Rh. Additional features occur in the C1s and N 1s spectra indicative of the formation of other forms of N and C, as yet unassigned. If CO is dosed and dissociated first, then CO@sub 2@ is not formed upon subsequent exposure to NO. However, the features associated with the unassigned, adsorbed species do appear upon annealing. The only products observed in thermal desorption are CO and N@sub 2@ and, in particular, no CO@sub 2@ is desorbed. Additional experiments are in progress to identify the unassigned species and to determine the mechanisms of their formation. * Research was sponsored by the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy at Oak Ridge National Laboratory, managed by Lockheed Martin Energy Research Corp. under contract number DE-AC05-96OR22464.

3:40pm **SS2-MoA6 Non-linear Behaviour in the NO-H@sub 2@ Reaction over Pt Group Metals: A Comparison***, **C.A. de Wolf**,* Leiden University, The Netherlands*; M.Yu. Smirnov,* Boreskov Institute of Catalysis, Russia*; M.O. Hattink, B.E. Nieuwenhuys,* Leiden University, The Netherlands

Oscillations in the NO+H@sub2@ reaction have been observed over the single crystal surfaces of Rh(533), Rh(311), Rh(111) and Pt(100).@footnote 1@ The following N-containing products can be formed: N@sub2@, NH@sub3@ and N@sub2@O. Recently, we observed oscillations over Ir(110)@footnote 2,3@ and Ir(210). The rate of N@sub2@ formation oscillates out of phase with the rate of NH@sub3@ and H@sub2@O formation. No N@sub2@O is formed. By using synchrotron radiation we could perform fast XPS measurements during a heat and cool cycle in the reaction mixture.@footnote 4@ These measurements show that there is a strong repulsive interaction between adsorbed N and O and that N builds-up on the surface during the NH@sub3@ formation. This information was used to propose a model for the oscillations in which the surface oscillates between an N covered surface which blocks the hydrogen adsorption and an O covered surface, which is accessible to hydrogen. A comparable model was suggested for Rh. However, the H@sub2@/NO ratio, the period and the shape of the oscillations are different for these metals. This is probably caused by differences in the rate of the various reactions that take place.

The NO+H@sub2@ reaction over Ru(0001) shows a different picture. In this case hardly any NH@sub3@ is formed during a heat and cool cycle even under H-rich conditions and instead of a build-up of N a build-up of O on the surface was obtained. No oscillations have been observed so far. A comparison of the non-linear behaviour in the NO+H@sub2@ reaction of these various metals will be made. @FootnoteText@@footnote 1@N.M.H. Janssen, P.D. Cobden, B.E. Nieuwenhuys, J. Phys.: Condens. Matter 9 (1997) 1889-1917 @footnote 2@C.A.de Wolf, B.E.Nieuwenhuys, A. Sasahara, K.Tanaka, M.M. Slinko, M.Yu. Smirnov, Surf. Sci. 411 (1998) L904-L909 @footnote 3@C.A. de Wolf, B.E. Nieuwenhuys, M.M. Slinko, M.Yu. Smirnov, accepted for publication in the Proc. of IVC-14 to be published in Surface Science @footnote 4@C.A. de Wolf, S. Lizzit, A. Baraldi, M. Kiskinova, B.E. Nieuwenhuys, in preparation.

4:00pm **SS2-MoA7 Chemical Diffusion, Percolation, and Order-Disorder Transitions in a Model for CO-Oxidation with c(2x2)-O Ordering**, ***D.-J. Liu***, *E.W. James, J.W. Evans,* Iowa State University

Pattern formation during CO-oxidation on single crystal surfaces is mediated by the chemical diffusion of adsorbed CO in a disordered environment of coadsorbed relatively immobile oxygen. We analyze CO-diffusion in a lattice-gas models for this reaction which incorporates c(2x2) ordering of adsorbed oxygen,@footnote 1@ and thus preferential diffusion at higher oxygen coverages of CO along anti-phase boundaries between c(2x2)-O domains. This constitutes a novel type of problem involving transport in a disordered medium, where CO-diffusion is blocked by percolation of the c(2x2)-O domains. We further show that such percolation is strongly influenced by (but not necessarily coincident with) a c(2x2) order-disorder transition in the oxygen overlayer. The latter constitutes a non-equilibrium analogue of order-disorder transitions familiar in equilibrated adlayers with short-range repulsive interactions. Precise results characterizing diffusion, percolation, and the order-disorder transition are obtained from extensive Monte Carlo simulations. @FootnoteText@ @footnote 1@ Y. Suchorski, J. Beben, E.W. James, J.W. Evans, and R. Imbihl, Phys. Rev. Lett. 82 (1999) 1907.

4:20pm **SS2-MoA8 CO-oxidation Reaction as a Probe of Oxygen States at Oxygen-rich Ru(0001)**, ***A. Böttcher,*** Fritz-Haber-Institut der MPG, Germany

It has been demonstrated that the oxidation of a Ru(0001) surface proceeds via four well characterized stages:(a) chemisorption, (b) oxygen penetration, (c) interfacial growth, (d) lateral and scale growth. The physical properties of the resulting oxygen phases were determined by means of thermal desorption spectroscopy (TDS), ultraviolet photoionization spectroscopy (UPS(21.2eV)) and low energy electron diffraction (LEED). The CO-oxidation reaction as performed over oxygen-rich surfaces has been used as a sensitive probe of various oxygen states. The analysis of the integral yield and the reaction kinetics reveals four well distinguishable oxygen species which are characteristic for the consecutive oxidation stages. In the high temperature regime (T>550K) the very efficient reaction is limited only by the diffusion of oxygen atoms from the subsurface region toward the topmost layer. The activation energy for this limiting reaction step ranges from 0.1 to 0.3 eV. In the low temperature regime (T

4:40pm **SS2-MoA9 Metastable States of Nitrogen Atoms Adsorbed on Ru(0001)**, ***L. Diekhöner***, *H. Mortensen, A. Baurichter, A.C. Luntz,* Odense University, Denmark

There has been a tremendous amount of work in recent years in the study of nitrogen interacting with ruthenium, in part because of its possible role as an alternative ammonia catalyst. There is still considerable disagreement as to the maximum coverage of adsorbed N allowed on Ru surfaces. We report here a novel way to produce high coverage states of nitrogen atoms adsorbed on Ru(0001) using an atomic N atom beam for dosing. Low doses produces the well known low coverage overlayers. At higher atom beam doses, we find sequential fillings of several previously unknown higher coverage states on the surface, ultimately forming a maximum coverage of 1 ML N/Ru atom. A large decrease in Ru-N bond strength with N coverage is apparent in our results and is in good agreement with recent density functional calculations. A combination of these calculations and our experiments indicates that the higher coverage states are in fact metastable relative to associative desorption, stabilized only by an increase in the barrier between the gas phase and the adsorbed state with coverage as well. Independent confirmation of the higher barriers for the high coverage states was also obtained via laser induced thermal desorption (LITD). In these experiments the kinetic energy distribution of the N@sub 2@ formed in associative desorption was measured by time of flight (TOF) techniques. We find N@sub 2@ desorbing with high translational energy distributions, much higher than seen in earlier desorption experiments from low coverages. Preliminary analysis indicates barriers that are at least in excess of 1.5 eV.

5:00pm **SS2-MoA10 Atomic Scale Chemistry: Desorption of Ammonia from Cu(111) Induced by Tunneling Electrons**, ***L. Bartels,*** Columbia University*; M. Wolf,* Fritz-Haber-Insitut der Max-Planck-Gesellschaft, Germany*; T. Klamroth,* Freie Universität Berlin, Germany*; P. Saalfrank,* University College London, United Kingdom*; A. Kühnle, G. Meyer, K.-H. Rieder,* Freie Universität Berlin, Germany

Excitation experiments on individual ammonia molecules on Cu(111) were performed with a low-temperature scanning tunneling microscope (STM) at 15 K. It could be shown that multiple electronic excitation of ammonia molecules can lead to an excitation of their substrate bond sufficient to caues desorption of the molecules from the substrate. This frequently results in their transfer to the STM tip apex. Tunneling spectra acquired with bare metal tips at the adsorption site of ammonia are compared with spectra acquired with ammonia decorated tip apices. The dependence of the desorption yield on the tunneling current at different biases shows a change of the order of the desorption process which nicely correlates with the number of incomming electron energies necessary to make up the binding energy. Excitation with either polarity, i. e. electron and hole attachment, can cause desorption. The change of the net desorption yield at different biases can be related to the standard model of the tunnel junction. Hartree Fock calculations allow to deduce from spectroscopic data that the ammonia modified Cu 4s state near the Fermi edge is responsible for the desorption process.

Thin Films Division

Room 620 - Session TF+VM-MoA

Advances in Hard and Superhard Coatings II

Moderator: B. Holloway, College of William & Mary

2:00pm **TF+VM-MoA1 Characterization of PVD TiN/CN@subx@ and TiN/Si@sub3@N@sub4@ Multilayer Coatings**, ***Y.H. Chen***, *Y.W. Chung,* Northwestern University

TiN coatings are commonly used in various tribological applications for their wear resistance and inertness to steels. However, TiN coatings predominantly grow with a columnar grain structure. The columnar grain boundaries become the usual sites for crack initiation, resulting in earlier failure of TiN coatings (especially thick coatings). In our research, TiN/a-CN@subx@ and TiN/a-Si@sub3@N@sub4@ nanolayered superlattice coatings are developed to suppress the columnar structure. We used a-CN@subx@ and a-Si@sub3@N@sub4@ primarily to periodically interrupt and renucleate the growth of TiN. In addition, the amorphous layers may serve to suppress the transmission of dislocations from one TiN layer to another, thereby enhancing the hardness of the coating. Both coatings have been demonstrated to achieve hardness in the 50 GPa range, consistent with recent reports for high hardness of TiN/a-Si@sub3@N@sub4@ nanocomposites. The correlation between microstructure and mechanical properties of these coatings will be presented.

2:20pm **TF+VM-MoA2 Effects of Interface Mixing on Adhesion of Amorphous Carbon Films Synthesized by Variable-Energy Direct Carbon Ion Beam Deposition**, ***M.H. Sohn***, *S. Kim,* SKION Corporation

Using a variable-energy direct carbon ion beam deposition technique, thin amorphous carbon films were grown on silicon substrate. Interface modification was performed using C@super -@ energies in the range of 300-500 eV prior to the growth of the film to enhance adhesion of the film. By lowering the energy of the C@super -@ beam to 150 eV, amorphous carbon film was continuously grown after the interface modification. High-resolution electron microscopy illustrated that the silicon surface was severely damaged by 500 eV C@super -@ beam and the thickness of damage layer was about 15 nm. Carbon composition profile in silicon investigated by electron energy loss spectroscopy showed that 500 eV C@super -@ beam implanted carbon into silicon up to 30 nm in depth and carbon was mixed with silicon at this implanted region. Silicon L-edge study at the C/Si mixed region found C-Si bonding formation only at the surface of silicon over 2-3 nm-thick layers. The damage layer or C/Si mixing was not observed at 300 eV C@super -@ beam modification. Wear testing found that strong adhesion occurred in samples modified at 500 eV, which indicated complete mixing at the interface. At 300 eV, modified samples exhibited delamination failure, which indicated inferior adhesion of the films.

2:40pm **TF+VM-MoA3 Synthesis of Diamondlike Carbon Films with Superlow Friction and Wear Properties***, **A. Erdemir**, O.L. Eryilmaz, G. Fenske,* Argonne National Laboratory

In this study, we introduce a new diamond-like carbon (DLC) film providing friction coefficients of 0.001 and wear rates of 10-9 to 10-10 mm3/N.m in inert gas environments (e.g., dry nitrogen and argon). The film was grown on steel and sapphire substrates in a plasma enhanced chemical vapor deposition system using a hydrogen-rich plasma. Employing a combination of transmission electron microscopy, electron diffraction, Raman spectroscopy, and electron energy loss spectroscopy, we explored the structural chemistry of the resultant DLC films and correlated these findings with their friction and wear mechanisms. The results of tribological tests under a 10 N load (creating an initial peak Hertz pressure of 1 GPa on steel test pairs) and at 0.2 to 0.5 m/s sliding velocities indicated that a close correlation exists between the friction and wear coefficients of DLC films and the source gas chemistry. Specifically, films grown in source gases with higher hydrogen-to-carbon ratios had the lowest friction coefficients and the highest wear resistance. The lowest friction coefficient (i.e., 0.001 on a sapphire substrate) was achieved with a film derived from a gas mixture consisting of 25% methane and 75% hydrogen. The wear-debris particles found in and around the wear scars and tracks were analyzed by Raman spectroscopy and FTIR to elucidate the wear mechanism of DLC films. @FootnoteText@ *Work supported by the U.S. Department of Energy under contract W-31-109-Eng-38.

3:00pm **TF+VM-MoA4 Optical Characteristics of Carbon Nitride: Relationship with Mechanical Behavior and Possible Fullerene-like Microstructure***, **V. Hajek**, D. Poitras, D. Dalacu,* Ecole Polytechnique, Canada*; A. Bergeron,* Optical Coating Laboratory Inc.*; L. Martinu,* Ecole Polytechnique, Canada*; K. Rusnak, J. Vlcek,* University of West Bohemia, Czech Republic

Crystalline @beta@-C@sub 3@N@sub 4@ was predicted to exhibit extreme properties, such as hardness, comparable to that of diamond. Although the synthesis of the crystalline metastable phase has not been fully confirmed yet, already prepared "amorphous" CNx films possess very attractive characteristics. In our earlier studies we have shown that these films possess high hardness (up to 30 GPa), high elastic recovery (up to 85 %), and interesting tribological behavior. Such films prepared at temperatures above 200 °C, using magnetron sputtering, are predicted in recent literature to possess a fullerene-like microstructure. In our recent work we suggested to extend this model to account for hydrogen incorporation: Excessive amount (> 1 at. %) of hydrogen in the films is believed to inhibit crosslinking between graphite-like planes containing carbon and nitrogen, and thus to hamper formation of the fullerene-like microstructure. In the present work we focus on the optical properties of CN@sub x@ films studied by spectroscopic ellipsometry and spectrophotometry. Different dispersion relations such as Sellmeier, Cauchy and Drude-Lorenz oscillator were used to determine optical constants n and k. The optical behavior is related to the film microstructure and the film fabrication conditions. CN@sub x@ layers were deposited on Si substrates by reactive DC magnetron sputtering of graphite target in nitrogen plasma at a substrate temperature of 600 °C and at a substrate bias ranging from -300 to -700 V. Films were found substoichiometric in nitrogen (from 12 to 24 at. %), and a concentration of hydrogen between 1 and 5 at. % was revealed by elastic recoil detection (ERD) analysis. Increased hydrogen content was accompanied by lower hardness, elastic recovery and adhesion, by higher electrical resistivity (from 20 to 970 @ohm@cm), by formation of C-H and N-H bonds (FTIR), and by higher optical transparency in the VIS and IR regions. The latter characteristics are related to the variation of optical bandgap which increases with hydrogen incorporation.

3:20pm **TF+VM-MoA5 Preparation and Properties Enhancement of Silicon Carbonitride Films Using Reactive Magnetron Sputtering***, X.-M. He, K.C. Walter, **M. Nastasi**,* Los Alamos National Laboratory

Silicon carbonitride (Si(C,N)) films were synthesized on Si (100) and metal substrates by reactive d.c. magnetron sputtering with Ar as the sputtering gas and N@sub 2@ as the reactive gas. The composition and properties of the films were studied with respect to the influences of the bias voltage applied to substrates, the deposition temperature, and the gas flow ratio of N@sub 2@ to Ar (or F@sub N2@/F@sub Ar@). The Si(C,N) mechanical properties, hardness, fracture, and tribological properties, were observed to be highly depended on the processing conditions such as substrate temperature, the arrival ratios of ion to deposition atom, J@sub i@/J@sub a@, the negative bias voltage and F@sub N2@/F@sub Ar@. Under optimum conditions amorphous coatings with high wear resistance and harnesses as high as 40 GPa were prepared. The role of synthesis parameters on the structure, compositions, and mechanical properties will be discussed in detail.

4:00pm **TF+VM-MoA7 Bonding Structure and Optical Properties of Si-doped Diamond-like Films Synthesized by Plasma Immersion Ion Processing***, **X.-M. He**, K.C. Walter, M. Nastasi,* Los Alamos National Laboratory

Silicon-doped diamond-like carbon (DLC) films were prepared on Si(100), glass, and PMMA (polymethyl methacrylate) substrates at room temperature by using C@sub 2@H@sub 2@-SiH@sub 4@-Ar plasma immersion ion processing (PIIP) and their compositions were modified by changing deposition parameters of the gas composition and the negative bias voltages applied on the substrates. The influence of the Si dopant on the bonding structure and the properties of the DLC films were investigated by using ion beam analysis techniques, Raman shift, infrared spectroscopy, and by analyzing the measured density and hardness. The electrical and optical properties of Si-doped DLC films have been evaluated by the study of the electrical resistivity, the refractive index, the absorption coefficient, and the optical gap energy for the films. It was found that the variation of Si dopant was highly correlated with the changes of chemical bonding structure and properties. The careful control of gas flow ratio of C@sub 2@H@sub 2@ : SiH@sub 4@ : Ar in low pressure PIIP was needed for the growth of DLC films with optimal combinations of increased sp3 bonding structure, high hardness and density, and improved optical properties. The resultant Si-doped DLC films with a Si content up to 28 at % exhibited a higher optical transmittance in the visible light range. The tribological tests of Si-doped DLC films were carried out using a pin-on-disk tribometer in ambient air at about 15% relative humidity. The results shown that Si-doped DLC films exhibited a low friction coefficient of 0.03-0.08 and an enhanced wear resistance despite of deposition of the films on Si (100), glass, or PMMA substrates. The effects of ion impingement during PIIP deposition on the formation of Si-incorporated DLC films were discussed.

4:20pm **TF+VM-MoA8 Surface Acoustic Wave Propagation Properties of Nitrogenated Diamond-like Carbon Films***, **J.Y. Kim**, H.J. Chung, H.J. Kim,* Seoul National University, Korea*; H.M. Cho, H.K. Yang, J.C. Park,* Korea Electronics Technology Institute

Surface acoustic wave (SAW) devices have become more important as mobile telecommunication systems need high-frequency, low-loss, and down-sized components. Higher-frequency SAW devices can be more easily realized by developing new high-SAW-velocity materials. The ZnO/diamond/Si multilayer structure is one of the most promising material components for GHz-band SAW filters because of its high SAW velocity above 10,000 m/sec. Recently, DLC films are also considered to have a potential for this application, since their physical properties, such as hardness and elastic modulus, are comparable with those of diamond. However, the residual stress during deposition is an obstacle to this application, because the film having high residual stress could not sustain during the full fabrication process of SAW devices. Recently, there have been many reports of the nitrogenated DLC films, which is mainly driven by the possibility of realizing the superhard @beta@-C@sub3@N@sub4@ phase. Some researchers reported the residual stress reduction by nitrogen incorporation without any other significant change in film mechanical properties. In this study, nitrogenated (a-C:N) films were deposited by reactive sputtering method. The a-C:N film properties were investigated using Raman spectroscopy, FT-IR, AES, and x-ray reflectivity (GIXR). To investigate the SAW propagation characteristics of the a-C:N films, SAW filters were fabricated using interdigital transducer electrodes between the ZnO layer and a-C:N/Si(100), which were used to excite surface acoustic waves. SAW velocities were calculated from the frequency-response measurements of SAW filters. A generalized SAW mode with velocities between 5,000 m/s and 7,000 m/s were observed as well as a high velocity Pseudo-SAW mode with 14,000 m/s. We also calculated the film elastic constants from SAW propagation velocities in the layered structure.

4:40pm **TF+VM-MoA9 High Deposition Rate Diamondlike Carbon Films Deposited using Permanenet Magnet Electron Cyclotron Resonance Plasmas***, **C. Doughty**, J.B. Bailey,* ASTeX PlasmaQuest

We report deposition of hard diamondlike carbon films at deposition rates exceeding 500 nm/min using permanent magnet ECR plasma CVD. These films are characterized by high hardness ~10-20 GPA and stresses ~300-500

MPa. The deposition rates obtained exceed typical values for plasma CVD deposition by a factor of 10-50 and enable a range of novel applications including economically attractive deposition of >10-um-thick films. These films have electrical resistivities ~10^12 ohm cm at 1 MV/cm, and optical bandgaps ~2 eV. Index of refraction can be controlled over the range 1.7 - 2.2 by manipulation of the deposition parameters. Film hardness has been measured by nanoindentation and will be reported as a function of deposition parameters. Adhesion promoting processes have been developed and films exceeding 5 um thickness have been deposited on silicon, glass and stainless steel substrates without delamination failures. Thin films (

5:00pm **TF+VM-MoA10 Polymerization in Remote Hydrocarbon Deposition Plasmas***, A. de Graaf, M.F.A.M. van Hest,* ***M.C.M. van de Sanden****, K.G.Y. Letourneur, D.C. Schram,* Eindhoven University of Technology, The Netherlands

The chemistry of expanding argon plasmas into which either methane (CH@sub 4@) or acetylene (C@sub 2@H@sub 2@) is injected for fast deposition of a-C:H, DLC and diamond films was studied by means of mass spectrometry, Fourier transform infrared absorption and in situ ellipsometry. The measurements reveal that the plasma chemistry of the expanding Ar/C@sub 2@H@sub 2@ and Ar/CH@sub 4@ plasmas is dominated by argon ion induced dissociation of the precursor gas. For acetylene injection the ion-induced dissociation is very efficient leading to complete depletion under certain conditions. For methane injection however, even under conditions of highest reactivity 100% dissociation of the precursor gas can not be reached. In an Ar/CH@sub 4@ plasma under certain conditions up to 40% of the injected precursor flow is transformed into C@sub m@H@sub n@ (m>1) polymers. In an Ar/C@sub 2@H@sub 2@ plasma the polymerization is much less (maximum 4%) and preferentially C@sub 2m@H@sub n@ polymers are formed. This suggests that in an Ar/C@sub 2@H@sub 2@ plasma the C@sub 2@H radicals are the main building blocks in the polymerization process and that they are probably also the dominant radicals in the deposition process. In the case of acetylene injection the deposition rate as measured in situ by ellipsometry is proportional to the depletion of the precursor gas. For methane injection however this proportonality does not hold even when the polymerization is taken into account. The difference in the polymerization rate and the dependence of the deposition rate on the gas depletion for the two plasmas is attributed to the different loss probabilities of the radicals formed in the dissociation. It is suggested that the large amount of C@sub 2@H@sub 2@ formed in the Ar/CH@sub 4@ plasma may lead to formation of radicals which, due to their relatively high loss probability, may become the dominant growth precursors.

Thin Films Division
Room 615 - Session TF-MoA
Fundamentals and Applications of Ionized PVD

Moderator: F.K. Urban III, Florida International University

2:00pm **TF-MoA1 Plasma Interaction Effects in Ion-Beam Assisted Pulsed Laser Deposition of Al-O-N Films***,* ***A.A. Voevodin****, J.G. Jones, J.S. Zabinski,* Air Force Research Laboratory

Interactions between plasmas produced by a nitrogen ion-beam source and pulsed laser ablation of Al@sub 2@O@sub 3@ were studied. Plasma fluxes from both sources intersected on the substrate surface in a typical arrangement for ion-beam assisted pulsed laser deposition (AIPLD). The study was focused on the detection of temporal and spatial plasma distributions, excitation states, and chemical reactions in the substrate vicinity, which were not present when operating each of the plasma sources separately. Plasma emission imaging and spectroscopy analyses using an ICCD camera and a spectrometer were used to investigate plasma development and chemistry in real time using the initial laser pulse for synchronization. In the study, the N@sub 2@ background pressure was varied in the range from 0.08 to 4 Pa and X-ray photoelectron spectroscopy was performed for Al-O-N films. Film elemental compositions were correlated with plasma chemistry. Two significant plasma interaction effects were discovered. One resulted in a considerable activation of N and O and formation of NO in a near substrate region, which then reacted with Al to from Al-O-N. A maximum plasma excitation was observed at reduced 0.1-0.2 Pa N@sub 2@ pressures and provided the highest amount of N in the films. Above 1 Pa of N@sub 2@, the Al-O-N films had lower nitrogen content, even though more nitrogen was available for the deposition. Another interaction effect was observed in the 2-4 Pa pressure region, when formation of short lived plasma channels connecting ion-beam and laser ablated plasmas were detected. These channels resulted in plasma bending and shifting from the substrate surface, affecting film composition and influencing ion beam current extracted from an ion beam-source. The study suggested that the interaction of ion-beam and laser ablation plumes in IAPLD might considerably affect plasma chemistry, excitation stages, and spatial distribution, providing new opportunities for the control of resulting film properties. @FootnoteText@ Key words: ion-beam assisted pulsed laser deposition, plasma chemistry, Al@sub 2@O@sub 3@ ablation, aluminiumoxynitride.

2:20pm **TF-MoA2 Time-of-Flight Measurements of Sputtered Species using Novel Pulsed High Plasma Density Magnetron Discharge***,* ***K. Macák****, V. Kouznetsov, J.M. Schneider, U. Helmersson,* Linköping University, Sweden*; I. Petrov,* University of Illinois, Urbana

Time resolved plasma probe measurements of a novel high power density pulsed plasma discharge are presented. Extreme peak power densities in the pulse (on the order of several kW.cm@super -2@) result in a very dense plasma with ionic flux densities of up to 1 A.cm@super -2@ at source-to-substrate distances of several cm and at a pressure of 0.13 Pa. The pulse duration was ~50 µs with a pulse repetition frequency of 50 Hz. The plasma consists of metallic and inert gas ions, as determined from time resolved Langmuir probe measurements and in situ optical emission spectroscopy data. The influence from the process parameters on the temporal development of the ionic fluxes is discussed. Deconvolution of metal ion probe current pulse waveform allowed for the calculation of the average ion energy. The ionized portion of sputtered metal flux was found to have an average energy of 2.6 eV in the absence of gas scattering. The obtained energies of the arriving metal ions conform with the collisional cascade sputtering theory. The degree of ionization of the sputtered metal flux at a pressure of 0.13 Pa was found to be 40±20 % by comparing the total flux of deposited atoms with the charge transferred by metal ions in the pulse.

2:40pm **TF-MoA3 Modeling of I-PVD Systems for TiN Film Deposition in Inductively Coupled Plasmas***,* ***M. Li,*** University of California at Berkeley, CANADA*; D.B. Graves,* University of California at Berkeley

TiN films are widely used as a diffusion barrier for aluminum, tungsten as well as copper in VLSI fabrication. Recently, ionized metal physical vapor deposition, or IPVD, has been used for TiN film deposition. However, this reactive sputtering process is relatively poorly understood. In this work, a two dimensional hybrid model, including a Monte Carlo treatment of fast sputtered atoms from the target and a fluid plasma simulation, is developed to study TiN film deposition in IPVD tools. The model includes a site balance surface model to describe the film deposition and target sputtering processes. Important issues such as neutral gas heating and rarefaction, the uniformity of film deposition across the wafer, and the film deposition characteristics have been investigated. In particular, the model predicts that the titanium species profiles and target shape are major factors in film deposition and computational uniformity at the substrate. The simulation results have been compared to the available experimental measurements.

3:00pm **TF-MoA4 Origin and Evolution of Sculptured Thin Films***,* ***R. Messier****, V.C. Venugopal, P.D. Sunal, H. Maeda,* Penn State University **INVITED**

Sculptured thin films (STFs) are columnar thin films prepared by directed vapor deposition under low adatom mobility conditions. Since the columns grow in the direction of the incoming vapor, and this column direction can be changed instantaneously, a new class of thin films can be engineered in which the STF nanostructural shapes can be sculptured into useful morphologies such as helices, matchsticks, chevrons, and periodically bent nematics. Wide variations in the exact STF shapes, as well as combinations of these morphologies, are possible through simple rotations of the substrate around two canonical axes. Potential applications include optical retardation layers for use in optical storage and communications systems, optical sensors for fluids of biological, chemical or nuclear significance, templates for biomaterials growth, and low-pemittivity materials for microelectronics. For normal angle deposition the columns generally expand and compete for growth evolution, thereby resulting in a cauliflower-like morphology. This is due to an in-plane, isotropic, atomic self-shadowing mechanism. Fortuitously, for large oblique angle deposition conditions („ 40š vapor incidence angle with respect to the substrate normal), typical for STF preparation, the columns become slanted, separated, and cylindrical due to an anisotropy in the self-shadowing process. Thus, the columns have a constant cross-section with film evolution - a requirement for many practical applications. It has been found experimentally, however, that under conditions of rapid or abrupt rotation of the substrate during oblique angle deposition, the columns expand, a situation which could limit their utility. In order to control STF morphology in the broadest sense, it is necessary to understand the details of the atomic clustering and growth competition process. In this paper a fundamental and yet practical approach will be presented for classifying the atomic self-shadowing processes in STF growth based upon previous experience in morphology evolution modeling and experiments. Recent experiments in STF growth include systematic changes in column growth rate / substrate rotation rate, use of textured substrates, and variations of low energy ion bombardment.

3:40pm **TF-MoA6 Ionized Physical Vapor Deposition (PVD) using Hollow-Cathode Magnetron (HCM) Source for Advanced Metallization***, **E. Klawuhn**, G.C. D'Couto, K.A. Ashtiani, P. Rymer, M.A. Biberger, K.B. Levy,* Novellus Systems, Inc.

Ionized Physical-Vapor Deposition (I-PVD) has been recognized as the technology of choice for extending the application of PVD processes to < 0.25 µm device geometries. However, due to the complexity of the conventional RF I-PVD, these sources are not in widespread manufacturing use. The Hollow-Cathode Magnetron (HCM) source is a new and promising technology that maintains the simplicity of the PVD technology and combines it with a very high-density diffused plasma (> 10@super 12@ #/cm@super 3@) for efficient ionization of sputtered metals. The HCM is based on the principle of charged particle magnetic mirror applied to an inverted cup shaped target. As such, it does not require any additional RF or microwave sources for generation of metal ions. The HCM source was used for deposition of Ti(N), Ta(N), and Cu films. Excellent bottom coverage (20 % for Cu, 40% for Ta and 30 % for Ti) in narrow, high aspect ratio vias (0.25µm, 5:1 AR) was obtained without the application of RF bias to the wafer. Since reactive processes were run in a non-poisoned mode, both TiN and TaN films had the same step coverage as Ti and Ta films, respectively. The TiN film resistivity is of the order of 30 µ@ohm@-cm (for a 1000 Å film) and close to the theoretical bulk resistivity of 18 µ@ohm@-cm. The HCM films have strong crystallographic orientation, and for Ti, TiN, Ta, and Cu respectively. RF bias was utilized to increase the bottom coverage and the sidewall coverage of the films, thus extending the technology to higher aspect ratios. In addition, RF bias was used to modify film properties such as grain size, grain orientation, and film texture. In this paper, the HCM theory of operation will be reviewed and results will be presented for the application of this source for deposition of Ti(N), Ta(N), and Cu films. In addition, the effects of RF bias on step coverage and film properties will be discussed.

4:00pm **TF-MoA7 Gas Phase Dynamics of Copper Ionized Metal Plasmas***, **Y. Andrew**, I.C. Abraham, Z. Lu, T.G. Snodgrass, A.E. Wendt, J.H. Booske,* University of Wisconsin, Madison*; P.L.G. Ventzek, S. Rauf,* Motorola

Copper ionized metal plasmas are of interest for the Damascene process of interconnect fabrication, in which trench and via structures are filled with copper. Used to deposit seed layers for subsequent electroplating, ionized metal plasmas produce films with enhanced conformality compared to conventional physical vapor deposition (PVD) processes. Improved understanding of the performance potential and limitations of this process motivate this study to characterize discharge properties through experiment and simulation. We examine a system consisting of a DC powered 15 cm D copper sputter source and an RF induction plasma powered by a single turn 36 cm D loop antenna internal to the vacuum chamber, with an argon pressure of 10-50 mTorr. Measurements include plasma parameters, ion and neutral copper flux at the substrate, RF and DC potentials on the antenna and in the plasma, and spectroscopic measurements of ground state and metastable copper as well as argon metastable concentrations in the gas phase. The simulations have been done using the Hybrid Plasma Equipment Model, a comprehensive plasma equipment modeling tool developed at the University of Illinois. The plasma is treated as a fluid in this model except for thermal copper neutrals sputtered from the target, for which a Monte Carlo simulation is used. The extensive data set includes some surprising observations. For example, both experiment and simulation show that for some operating conditions, the copper metastable density is substantial compared to that of the ground state population. Measurements and simulation will also address electrical measurements on the system, including a substantial but unexpected DC self-bias voltage on the antenna. Finally, by comparing copper fluxes measured directly and computed from spectroscopically determined gas phase concentrations, we can infer the temperature of the copper in the gas phase, which is found to increase substantially with RF power to the plasma.

4:20pm **TF-MoA8 Effects of Copper Seedlayer Deposition Method for Electroplating***, **E.C. Cooney III**, D.C. Strippe, J.W. Korejwa,* IBM Microelectronics

We have investigated copper seedlayer deposition using both ionized PVD and collimation methods by depositing similar films into agressive dual damascene structures. Step coverage measurements using TEM indicated that ionized PVD seedlayers exhibited better bottom and sidewall coverage than collimated seedlayers. Subsequent electroplating of contact structures did not indicate differences in the quality of the filling when observed using SEM. However electrical testing of 68000 dual damascene via chains did show improved chain yield for the ionized PVD deposited films. Cross-sections of the chains revelaed small voids at the bottom of the vias deposited using collimated seedlayers while no voiding was observed for the ionized PVD copper films. Finally SEM examinations of unfilled dual damascene cross-sections indicated the ionized copper seedlayers to be rougher as compared to copper films sputtered using collimation.

4:40pm **TF-MoA9 Steel Coating by Self-induced Ion Plating, a New High Throughput Metallization Ion Plating Technique***, **P. Vanden Brande**, A. Weymeersch,* Cockerill Sambre - RDCS, Belgium

Ion plating techniques present major advantages for continuous steel coating in terms of throughput and product quality when compared respectively to sputtering and vacuum evaporation techniques. However, the ion plating systems available on the market today are still cumbersome and present technological difficulties for immediate implementation in high throughput air-to-air continuous steel coating plants. To address these difficulties we have developped a new ion plating technique referred to as self-induced ion plating in order to produce continuous coating on flat products. This technique is essentially based on the generation of a magnetron discharge in the sputtered and evaporated vapour produced by a tin cylindrical target. Very high deposition rates were achieved (220µm/min) with moderate values of the electrical mean power density (45W/cm@super 2@) applied to the tin target. The magnetron configuration used allowed the reduction of material side losses. This was achieved by reducing the metal escape zone area on the target side. Another feature of this technique is that the control of the heat transfer between the target and its backing plate allows the control of the target surface temperature and hence the control of the sputtered and evaporated material fractions.

5:00pm **TF-MoA10 Analysis of Mode Transistions in I-PVD and Conventional PVD Reactive Sputtering of Refractive Diffusion Barrier Materials***, D.R. Juliano, R. Ranjan, D.N. Ruzic, **J. Norman**,* University of Illinois, Urbana-Champaign

I-PVD techniques have shown to be effective for the deposition of contact, barrier, adhesion and seed layers. For copper metallization such layers include Ti, Ta, TiN and TaN. In conventional PVD processes, reactive sputtering techniques have shown two important deposition modes, namely, metallic and poison modes. In the metallic mode the nitration occurs on the substrate whereas in the poison mode it occurs on both the target and the substrate. There are advantages and disadvantages of each. Mode transitions are compared between I-PVD and conventional PVD sputtering processes. The analysis includes measurements of plasma temperature and density using Langmuir probe techniques, as well as ionization fractions and deposition rates. A dc planar magnetron with a 33-cm diameter target is coupled with a secondary plasma source to ionize the sputtered metal neutral flux to control the angular distribution of the flux arriving at the surface of the substrate. The secondary radio-frequency (rf) plasma is created between the sputtering target and the substrate by a multi-turn coil located in the vacuum chamber. The rf plasma increases the electron temperature and density, which results in significant ionization of the neutral metal flux from the sputtering target. By applying a small negative bias to the substrate, metal ions are drawn to the substrate at normal incidence. 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.

Organic Electronic Materials Topical Conference
Room 4C - Session OE-MoP
Poster Session

OE-MoP1 STM/Photo-Assisted EFM Investigation of Morphology-Photoconductivity Relationships in Photogenerating Dye Molecule Thin Films*, M.E. Stawasz*, *N. Takeda, B.A. Parkinson,* Colorado State University

STM and photo-assisted EFM (Electric Force Microscopy) were used to study the relationship between morphology and photoconductivity for a photogenerating dye molecule used commercially in photoreceptor devices. Bis(4-dimethylamino-2-hydroxyphenyl) squaraine was adsorbed from solution onto the basal plane of HOPG. Several polymorphs of adsorbate structure were determined with STM. EFM coupled with a 0.5W 690nm diode laser to illuminate the sample surface was used to spatially resolve areas of differing polymorph in terms of their differing photoconductivity. By identifying regions of differing polymorph, then measuring the relative photoconductivities of each phase a polymorph structure-photoconductivity relationship was identified.

OE-MoP2 Ordered Thin Film and Organic Heterojunction Formation from Luminescent Organic Dyes*, D.M. Alloway*, *N.R. Armstrong,* University of Arizona*; A. Back,* Physical Electronics*; B. Schilling,* VG Micromass

Perylenes, phthalocyanines, certain quinacridones, and related dyes can be vacuum deposited to form ordered monolayers and multilayers. The ordering in these monolayers can be monitored with electron diffraction techniques, and scanning probe microscopies (STM/AFM), but we have recently also found that luminescence spectroscopies can be used to follow the nucleation and growth of the first monolayer, and subsequent multilayer formation. This paper will focus on recent studies of the growth of perylenetetracarboxylicdianhydridebisimide (PTCDI) dyes (both C4 and C5 tails on the bisimide), and substituted quinacridones on both single crystal metal and nonmetal surfaces. Layered growth is seen in all multilayer films, with flat-lying monolayers apparently formed in most cases, and where the structure of the 2nd and subsequent layers is strongly dependent upon the stable bulk structures for these materials. Luminescence spectroscopies indicate the degree of cofacial interaction between these dyes, during monolayer nucleation, and as layer-by-layer growth is achieved. For certain quinacridone dyes the substituent side chains control the approach distance of adjacent molecules, significantly altering the luminescence spectra relative to the parent molecule. In addition, luminescence spectra are useful in characterizing the degree of interaction between two dissimilar dyes, at the organic/organic' interface in a heterojunction assembly, and the degree of luminescence quenching appears to correlated with interface dipole formation as indicated by XPS/UPS studies.

OE-MoP3 Contact Resistance Measurements on Individual Grains of @alpha@-Sexithiophene*, A.B. Chwang*, *C.D. Frisbie,* University of Minnesota

We describe four point probe measurements on individual grains of the molecular semiconductor sexithiophene (6T). These measurements utilize thin 6T grains (2-14 nm in thickness and 1-2 µm in length and width) deposited by vacuum sublimation onto SiO@sub 2@/Si substrates previously patterned with sets of four closely spaced (<400 nm) Au electrodes. The 6T grains grow between the four contacts and their electrical behavior is probed as a function of temperature and gate voltage applied to the substrate. From these data, we extract the Au-6T contact resistance and determine its sensitivity to both gate field and temperature.

OE-MoP4 Electronic Transport Properties of Self-assembled @pi@-conjugated Azomethine Oligomers*, J.J.W.M. Rosink*, *L.J. Geerligs, E. van der Drift,* Delft Institute of Microelectronics and Submicrontechnology, The Netherlands*; A.I. Onipko,* Bogolyubov Institute for Theoretical Physics, Ukraine*; Y. Klymenko,* Space Research Institute, Ukraine*; B.A.C. Rousseeuw,* Delft Institute of Microelectronics and Submicrontechnology, The Netherlands*; S. Radelaar,* Netherlands Institute for Metals Research, The Netherlands

A novel technique for the controlled fabrication of @pi@-conjugated azomethine oligomers bonded to a substrate is presented. The resulting thin films can be used to study the intra-molecular electronic transport properties. Starting from a gold substrate, monolayers of small monomeric organic units are alternately deposited from solution. They order and connect to the previous layer by self-assembly. In each deposition step, chemisorption takes place at the interface between two monolayers through a condensation reaction. Oligomer chain growth has been analyzed by ellipsometry, gaschromatography, mass-spectrometry and x-ray photoelectron spectroscopy (XPS). Molecular mechanics calculations support the observation from ellipsometry and XPS that the azomethine molecules order roughly perpendicular to the gold surface. Based on scanning tunneling spectroscopy (STS) experiments an electronic model for these experiments is proposed. The Green function method is used to establish the relationship between the I-V curves registered in the STS measurements and the @pi@-electronic structure of the oligomers of type M@sub 1@-M@sub 2@-M@sub 1@... probed in the experiments. We have succesfully fitted I-V curves observed in STS of a single monomer film. Modelling of organic multilayers with a particular focus on the role of molecule-to-metal contact is in progress.

OE-MoP5 Perfluorinated Alkane Self-assembled Monolayers Studied with XPS and ISS*, D.E. King*, *A.W. Czanderna,* National Renewable Energy Laboratory*; L.S. Dake,* Susquehanna University

Perfluorinated Alkane Self-assembled Monolayers Studied with XPS and ISS D.E. King, A.W. Czanderna, and L.S. Dake* National Renewable Energy Laboratory, MS-3214 1617 Cole Blvd. Golden CO 80401-3393 The purpose of our past work has been to use self-assembled monolayers (SAMs) as a model organic surface for studying the interactions and penetration of deposited metals on or through specific organic functional groups of the SAMs.@footnote 1@ Our future goal will be to study the interactions, reactions, and stability of deposited metals and metal oxides on SAMs, but in a simulated solar environment, e.g., UV irradiance, T to about 333 K, and in the presence or absence of humidity. Because we expect UV degradation to complicate studies with the n-methylene groups (6<n<21) in alkanethiols in our past work,@footnote 1@ we are reporting our feasibility studies with perfluorinated alkane (PFA) SAMs. We will discuss our approach for the assembly of PFASAMs by using an acid attachment group instead of a thiol and demonstrate the presence of a single monolayer film. We have characterized the PFASAMs by contact angle, XPS, and ISS. The erosion rates in ISS for PFASAMs of different chain-length and with several different end groups will be discussed as they relate to macroscopic film properties such as the contact angle. The stability of the PFASAMs during X-ray exposures will also be compared with results of similar chain-length alkanethiols. @FootnoteText@@footnote 1@D.R. Jung, G.C. Herdt, and A.W. Czanderna, J. Vac. Sci. Technol., A14 (1996) 1779. This work was performed under DOE Contract No. DE-AC36-98GO10337.

OE-MoP6 Resonant Photoemission Study of Poly(p-PhenyleneVinylene)*, Y. Park*, Korea Research Institute of Standards and Science, KOREA*; Y. So,* Korea Research Institute of Standards and Science*; G.S. Lee,* Korea Research Institute of Standards and Science, Korea*; E. Cho,* Chonnam National University, Korea

We have employed synchrotron radiation resonant photoemission technique to investigate the electronic structures of one of the prototype organic electroluminescent polymer Poly(p-PhenyleneVinylene) (PPV). When the photon energy was near the binding energy of C 1s core level, at least three strong resonacnes at the approximate binding energies of 5, 6.5, and 9 eV could be observed We discuss the origin of the observed resonances and identify the symmetries of related valence energy levels. The results of resonance photoemission on Ca-induced gap states formed in near-surface region of PPV thin film were also discussed.

OE-MoP7 Investigation of the Influence of LiF-Coatings on the Electronic Structure of Organic Semiconductor/Electrode Interfaces by Photoemission Spectroscopy, *R. Schlaf,* State University of New York at Binghamton*; **P.A. Lee**, K.W. Nebesny, N.R. Armstrong,* University of Arizona

Recently, it was demonstrated that the performance of organic light emitting diodes (OLED) can be considerably improved by inserting thin (~1nm) LiF layers between charge injecting electrodes and organic semiconductor layers. We have determined the electronic structure of typical metal/LiF interfaces with photoemission spectroscopy (PES). In our experiments LiF thin films were grown in multiple steps on sputter-cleaned Al, Pt and ITO substrates. Before growth of the LiF films and after each LiF deposition step the samples were characterized in-situ by combined X-ray and UV photoemission spectroscopy (XPS, UPS) measurements. Our results suggest that the LiF coatings considerably lower the work function of the electrode surfaces, hence resulting in a much reduced electron injection barrier between low work function electrodes and organic electron transport materials. In the case of Al electrodes a surface dipole created by chemisorbed water emitted from the LiF evaporation source is partially responsible for the work function reduction observed after the LiF deposition. Our measurements also demonstrate that even in insulators such as LiF effects similar to band bending in semiconductors may occur.

The results suggest, that a redistribution of charged Schottky or Frenkel type defects in the LiF layers, caused by the thermodynamic equilibration between LiF and the contact metal, is possibly responsible for the observed phenomena.

Plasma Science and Technology Division
Room 4C - Session PS-MoP
Poster Session

PS-MoP1 A-Si:H Film Deposition Using Plasma CVD with Suppression of Cluster-Size Particles, ***M. Shiratani**, S. Maeda, Y. Matsuoka, K. Tanaka, K. Koga, Y. Watanabe,* Kyushu University, Japan

In order to deposite high quality a-Si:H at a high rate using SiH@sub 4@ RF discharges, we have developed methods for suppressing cluster-size particles, which are believed to degrade film quality. We have examined effects of pulse modulation of discharges, heating of the GND electrode as well as H@sub 2@ dilution on growth of particles by using two novel in situ methods@footnote 1,2@ for determination of size and density of cluster-size particles below 10 nm in size. Even under so-called device qualtiy conditions, particles have begun to be observed around the plasma/sheath boundary near the RF electrode and mainly grow in the same region. They grow at a growth rate of 10 nm/s, much higher than a typical film deposition rate of 0.1 nm/s, and their density is above 10@super 10@ cm@super -3@. We also have studied effects of GND electrode heating on suppression of particles in modulated discharges. While the modulation without heating the GND electrode brings about suppression of particle growth, the modulation with heating the GND electrode to 200C realizes deposition without cluster-size particles during more than 1 hour even for a relatively high duty cycle of 63% (t@sub on@=5 ms). This notable suppression of particle growth with the heating can be explained by a model taking account of thermophoretic force exerted on particles. High H@sub 2@ dilution (>80%) has been revealed to be effective in suppressing growth of cluster-size particles especially around the plasma/sheath boundary near the RF electrode. Correlation between particle density and film quality will be presented. @FootnoteText@ @footnote 1@M. Shiratani and Y. Watanabe., Rev. Laser Eng., 26 (1998) 449. @footnote 2@T. Fukuzawa, et al., J. Appl. Phys., 80 (1996) 3202.

PS-MoP2 Surface Reactivities of Radicals in Fluorine Containing Plasmas, ***C.I. Butoi**, E.R. Fisher,* Colorado State University

Fluorocarbon plasmas have a variety of applications such as generation of interlevel dielectric films and etching in the microelectronics industry, as well as generation of polymeric biocompatible materials. Understanding deposition and etching mechanisms is a difficult task given the complexity of plasma systems. Using the imaging of radicals interacting with surfaces (IRIS) technique, we are able to investigate the behavior of one plasma species at a time. Hexafluoropropylene oxide (HFPO) has shown great promise for generating high CF@sub 2@ content films, and CF@sub 2@ radicals have been postulated as the main deposition precursors. Thus, studying the reactivity of CF@sub 2@ radicals impinging on surfaces is of the utmost importance in understanding film formation mechanisms. In the IRIS experiments, CF@sub 2@ spatially resolved LIF signals are collected and analyzed using a geometrical simulation of the experiment. Fitting the experimental data to simulated fits generates scatter values, S, for CF@sub 2@ radicals. S values less than 1 indicate loss of CF@sub 2@ moieties at the substrate surface, whereas S > 1 suggests surface generation of CF@sub 2@. In CW HFPO plasmas, S values of 1 were calculated for silicon based and polymeric substrates regardless of the rf power employed. Pulsed plasmas were also used and duty cycles were varied. A decrease in the CF@sub 2@ scatter coefficients was observed for both substrates tested at all duty cycles. Also, the CF@sub 2@ S values were determined when a grounded mesh was placed in the path of the molecular beam in order to probe the possible role of ions generated in the plasma. Decreases in S were observed under these conditions. To further investigate ion effects, silicon substrates were biased at +200V, which resulted in S 0.5-0.6. Additional results for plasma etching systems will be presented.

PS-MoP3 Studies on SiF@sub x@ Radicals in Fluorosilane Plasmas Used for Silicon Etching and Deposition, ***K.L. Williams**, C.I. Butoi, E.R. Fisher,* Colorado State University

Fluorosilane plasmas are used in the microelectronics industry for etching of Si/SiO@sub 2@ and for deposition of fluorinated silicon-based materials (a-Si:H,F). Currently, fluorinated a-Si films are used in the fabrication of solar cells, photoreceptors, and thin film transistors. In spite of such high quality film production, there is still controversy over the mechanistic aspects of etching and deposition processes. Moreover, fundamental chemical information on plasma species such as SiF@sub x@ radicals is not available. Here, the surface reactivity of SiF@sub 2@ radicals during plasma processing of a silicon substrate using the imaging of radicals interacting with surfaces (IRIS) technique is reported. The molecular beam sources are 100% SiF4, 90/10 SiF4/H2, and 50/50 SiF4/H2 plasmas. Preliminary results show scatter ratios of 2.36 ± 0.08, 2.78 ± 0.08, 2.79 ± 0.13, and 3.08 ± 3.08 ± 0.11 for 30 sccm, 80 W and 170 W, and 15 sccm, 80 W and 170 W, SiF@sub 4@ plasmas, respectively. Scatter ratios >1 indicate SiF@sub 2@ is generated at the surface. Significant decreases in SiF@sub 2@ scatter are observed for SiF@sub 2@/H@sub 2@ plasmas. With these plasmas, SiF@sub 2@ scatter ratios are 1.31 ± 0.08 (10% H@sub 2@, 80 W), 1.48 ± 0.10 (10% H@sub 2@, 170 W), and 2.44 ± 0.13 (50% H@sub 2@, 170 W). These results are correlated with data from surface characterization by Fourier transform infrared spectroscopy (FTIR) and profilometry of films deposited under various plasma parameters (applied rf power, pressure, and % H@sub 2@ addition), as well as optical emission spectra for the fluorosilane plasmas studied.

PS-MoP4 Boron Effects on SBT Etching with Ar/Cl@sub 2@/BCl@sub 3@ Plasma, ***J.W. Seo**,* Chung Ang University, Korea*; W.J. Lee, B.G. Yu,* ETRI, Korea*; K.H. Kwon,* Hanseo University, Korea*; G.Y. Yeom,* Sung-Kyun-Kwan University, Korea*; C.I. Kim, E.G. Chang,* Chung-Ang University, Korea

Among the ferroelectric thin films that have been widely investigated for FRAM(ferroelectric random access memory) applications, SrBi@sub 2@Ta@sub 2@O@sub 9@ thin film is appropriate to memory capacitor materials for its excellent fatigue endurance. However, very few studies on etch properties of SBT thin film have been reported although dry etching is an area that demands a great deal of attention in the very large scale integration of ferroelectric thin film capacitors for FRAM applications. In this study, inductively coupled plasma(ICP) etcher was used for high density plasma etching of SrBi@sub 2@Ta@sub 2@O@sub 9@/Pt/Ti/SiO@sub 2@/Si with Ar/Cl@sub 2@/BCl@sub 3@ gas chemistries. SBT thin film was prepared with sol-gel method. Etch properties, such as etch rate, selectivity and profile, were measured according to split process parameters including RF power, bias voltage, chamber pressure and gas mixing ratio. Chemical reaction and residue of etched surface was analyzed with XPS(X-ray photoelectron spectroscopy) and SIMS(Secondary ion mass spectrometry). Changes of chemical composition in the chamber was analyzed with OES(Optical emission spectroscopy). As mole fraction of BCl@sub 3@ varied, boron effects with respect to residue, selectivity and etched profile was investigated. SBT was dominantly etched by Ar bombardment. Selectivity to photoresist(PR) or SiO@sub 2@ increased as decreasing mole fraction of Ar gas. Additive BCl@sub 3@ enhanced selectivity, profile and relative etch rate. SEM(Scanning electron microscopy) was used for examination of patterned SBT thin film. Change of stoichiometry on the film surface is discussed by comparing with OES analysis.

PS-MoP5 Characterization of Inductively Coupled Discharges in C@sub 2@F@sub 6@ and CHF@sub 3@, ***G.A. Hebner**,* Sandia National Laboratories

The chloro-fluorocarbon gases C@sub 2@F@sub 6@ and CHF@sub 3@ are used in a number of microelectronic plasma processing systems for both oxide etch and surface passivation. To provide data on the fundamental plasma characteristics as well as plasma species, microwave interferometry has been used to measure the line integrated electron density, photodetachment spectroscopy was used to measure the negative ion density, and laser induced fluorescence (LIF) was used to measure the spatially resolved CF density. The measurements were performed in a GEC rf reference chamber with an inductive coil plasma source and rf wafer bias. Photodetachment measurements of the negative ions as a function of wavelength are consistent with the dominant negative ion being F-. Different trends between the negative ion density and the electron density show that the negative ion precursor species density depends on power, pressure and rf wafer bias, but not on the feed gas. By pulse modulating the plasma power, negative ion - positive ion recombination rates have been determined. Spatially resolved LIF measurements show the CF density peaking in the center of the C@sub 2@F@sub 6@ discharge but a more uniform radial distribution in CHF@sub 3@. CF density scaling with power, pressure, rf bias and surface material will be shown. This work was performed at Sandia National Laboratories and supported by SEMATECH and the United States Department of Energy (DE-AC04-94AL85000).

PS-MoP7 Antennas for Large-Area, Inductively-Coupled Plasmas*, M.M. Patterson,* University of Wisconsin, Madison, US*; A.E. Wendt,* University of Wisconsin, Madison

Uniform plasma processing for large and noncircular substrates motivates the examination of design alternatives to the standard spiral antenna for inductively coupled plasmas. In addition to being unsuited for rectangular substrates, scaling of the spiral design suffers from several complications including increased voltage requirements@footnote 1@ (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.@footnote 2@ Therefore, we explore the feasibility of low inductance, scalable alternatives to the spiral design. We have constructed several rectangular antennas, 20 cm by 30 cm, from straight conductor segments, including serpentine and ladder shaped configurations. In the ladder configuration, neighboring parallel antenna segments carry currents in the same direction, while in the serpentine configuration, neighboring segments carry currents in opposite directions. Langmuir probe measurements of the spatial profiles of plasma properties show significant differences in the magnitude and uniformity of plasma density in argon discharges produced by these antennas. We will also present results from a circular serpentine antenna. Finally, as a means of understanding the differences between the antenna configurations, we have created and will present a simple model of the interference between the electromagnetic fields of neighboring parallel antenna segments. @FootnoteText@ @footnote 1@Jaeger EF, Berry LA, et al, Physics of Plasmas 2(6), 2597 (1995). @footnote 2@Kushner MJ, et al, J. Appl. Phys. 80(3), 1337 (1996).

PS-MoP8 Optical Emission and Mass Spectroscopic Studies of Reactive Species in an ICP Based Neutral Source for Ashing Processes*, X.M. Tang,* *D.M. Manos,* College of William and Mary

In this paper, we report measurements of particle composition and flux in downstream neutral cleaning processes in a reflection-neutral source, with a comparison to pulsed plasma processes. For Ar, O@sub 2@, and CF@sub 4@ mixtures, species in the both the plasma source and neutral process region are characterized by electrostatic probes, mass spectrometry, and optical emission; in the downstream region, calorimeter (energy) probes, and a micro-torsion (momentum) balance are used to discriminate the ion, photon, and neutral fluxes. The rf power, gas composition, reflector bias, discharge pressure have been varied in this study. The results show that in the downstream region, for Ar + O @sub 2@ plasmas, neutral O atom density and flux increase with increasing power from 100 to 500 watts, and also increase with increasing pressure. Ion species, including atomic and molecular ions, decrease in the downstream region as power and pressure increase over the same range. Both optical emission and mass spectral results show that the ratio of O/Ar increases sharply as the rf power increases above 200 watts in our source. In this source, neutral translational energy is varied by variation of the bias on the reflector plate. A concern in such a source has been that the variation of reflector bias may alter the species ratios in the source. The results of this study show that this is not the case. Using the combined diagnostic set, we have been able to differentiate the energy flux contributed by neutrals, photons, and charged particles striking the substrates. Our quantitative measurements indicate that the neutral flux is somewhat higher than predicted by our earlier simulations. This paper reports refinements to the model@footnote 1@ required to account for these new measurements. @FootnoteText@@footnote 1@ C.A. Nichols and D. M. Manos, J. Appl. Physics, vol.80 No.5 P2463.sept. 1996.

PS-MoP9 Estimation of Surface Kinetic Parameters and 2D Simulation of InP Pattern Features during CH@sub 4@-H@sub 2@ Plasma Etching*, A. Rhallabi,* *L. Houlet, G. Turban,* University of Nantes, France

Dry etching pattern-transfer of III-V materials from resist mask is an essential process stage in the fabrication of optical devices because anisotropy and reproducibility are more ensured than that in wet etching as feature dimensions decrease. In this study, 2D model of InP etched surface profile under CH@sub 4@-H@sub 2@ plasma is developed. In order to move the InP etched surface, an improved string algorithm is applied. The surface is approximated by a series of nodes joined by straight line segments which define the surface elements or string. During the displacement of the etched surface, time step is controlled automatically to ensure a good stability of the surface profile. Langmuir adsorption and re-remission of radicals, spontaneous chemical etching and ion sputtering on both adsorbed and not adsorbed surface fraction are considered. The main difficulty to predict the etched surface features is the lack of the kinetic surface parameters. In this study, the etching kinetic parameters (sticking coefficient, etch coefficients on both adsorbed and no adsorbed surface fractions) of the InP surface are proposed by comparing the experimental and simulated etching rate curves as a function of the incident CH@sub 3@ flux. Least square optimization method is applied to deduce such estimated surface parameters. The simulation results show the effect of the plasma and surface kinetic parameters on the topography of the microscopic etched profiles.

PS-MoP10 Physical Characterization of the Etching of Low-k Hydrogen SilsesQuioxanes (HSQ) Dielectrics under Medium and High Density Plasma Conditions*, C.H. Low,* *H. Cong, P. Yelehanka,* Chartered Semiconductor Manufacturing Limited, Singapore

The interconnect technology ventures into the development of low-k inter-metal dielectrics integration, arising from the need to reduce interconnect delay.@footnote 1@ The evolution of new low-k dielectric materials posts challenges to the conventional oxide etching processes.@footnote 2@ Hydrogen SilsesQuioxanes (HSQ)-based Flowable-Oxide (FOx), similar in composition as conventional oxide while offering low k values of 2.9 - 3.0, is used as the low-k IMD materials in our studies. The direct-on-metal (DOM) approach is employed for the integration of FOx as IMD layer for sub-0.25 micron application.@footnote 3,4@ The FOx layer is further capped with a thick PETEOS film, preventing it from degradation when subjected to subsequent high temperature processing steps. The etching of FOx integrated IMD stack is carried out using both TEL 85 DRM medium density plasma etcher and LAM TCP 9100 high density plasma etcher with different fluorocarbon etch chemistry. The physical characterization of the etching of FOx IMD stack under both conditions is demonstrated. In both cases, the FOx IMD vias are successfully opened with reasonably straight profiles. While high density plasma etching posesses in-situ PR strip capability for process simplification, it is also shown to induce more Si-H loss in the FOx layer. On the other hand, less damage is introduced to the FOx layer when etching under medium density plasma condition. Etch rate studies of FOx film cured at different temperature and duration as well as the film properties changes upon etching are also investigated. This is for better understanding of the etch process capability when subjected to different film curing conditions. @FootnoteText@ @footnote 1@L. Peters, Semicon. Int'l, p.64, Sep. 1998. @footnote 2@T.E.F.M. Standaert et.al., Mat. Res. Soc. Symp. Proc., p.265, vol.511, 1998. @footnote 3@B.T. Ahlburn et.al., Conf. Proc. ULSI XI, p.67, 1996. @footnote 4@Technical notes from Dow Corning Corp..

PS-MoP11 Modeling and Experimental Characterization of a Ti/Nitrogen/Ar Ionized Physical Vapor Deposition Tool*, K. Tao,* *D. Mao, J. Hopwood,* 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. One method of directionally-depositing materials is ionized physical vapor deposition (IPVD). Sputtered atoms are ionized in IPVD by a high-density plasma and, subsequently, collimated toward the wafer by the plasma sheath potential. Although considerable work has been reported on the deposition of metal films using argon as the working gas, very little is known about reactive sputter deposition using IPVD. The formation of high quality metal-nitrides that exhibit high conformality is possible using a working gas of nitrogen and Ar. The Ti-Ar-N@sub 2@ plasma, for example, is used for the deposition of TiN. Reactive IPVD is being studied both experimentally and through analytical plasma modeling. The gas-phase densities of ionized, excited, and dissociated species of Ti, Ar, and nitrogen are predicted and compared with experimental measurements that include mass spectrometry, optical emission spectroscopy, and Langmuir probes. The dissociation of nitrogen is used to benchmark the model. Both the model and measurement show that the dissociation fraction lies between 5% and 20% and decreases with increasing plasma pressure. The effect of nitrogen on the degree of ionization of sputtered titanium, and therefore the bottom-coverage of high aspect ratio features, will also be discussed.

PS-MoP12 Influence of Dry Etching Gas Chemistry on the Formation of Line Edge Roughness of Patterned Oxide Hard Mask*, A.S.-Y. Li,* State University of New York at Albany

As the pattern feature size shrinks to sub-quarter micron, line edge roughness (LER) of hard mask becomes critical in line-width control for pattern transfer. The patterns with LER affect both device characteristics and electrical properties. Contributions to LER of resist have been carefully studied. However, understanding of dependence of LER on dry etching gas chemistry is still in the very early stage. LER of oxide hard mask has been observed after being patterned with deep UV (DUV) resist on a magnetically enhanced reactive ion etching tool, even though no LER was seen on DUV resist before hard mask patterning. Results show that the roughness depends very much on etching gas chemistry. Introduction of O@sub 2@ into process will cause very serious edge roughness, while CF@sub 4@ gas can reduce its formation on the line edge. Experiments also show that LER is first formed on the side wall of the resist and bottom anti-reflective coating layer, then it is transferred onto hard mask. Extending etching time will increase LER. Different etching behavior of gas chemistry has also been observed on resist. Top-view from critical dimension scanning electron microscopy shows a rough surface formed on resist after being etched using plasma containing either O@sub 2@ or Ar, but a much rougher surface has been seen on that from O@sub 2@ plasma. On the other hand, a combination of both Ar and O@sub 2@ plasma produces a very unform and smooth resist surface. Different etching behavior of gas chemistry, O@sub 2@, Ar, and CF@sub 4@ in hard mask opening is very helpful for us to understand the formation of the line edge roughness.

PS-MoP13 The Effect of Electrode Gap on CF@sub 2@ Distribution and Electrical Parameters in Fluorocarbon Plasmas*, **K.L. Steffens,** M.A. Sobolewski,* National Institute of Standards and Technology

Fluorocarbon plasmas are widely used by the semiconductor industry for etching and in situ cleaning of PECVD chambers. Previous studies in parallel-plate reactors have indicated that reactive species density distributions, precursor destruction efficiencies, plasma optical emission, and cleaning rates are correlated to the rf current measured at the upper, grounded electrode, I@sub ge@. In these studies, I@sub ge@ varied with changing pressure or was directly controlled by adjusting the impedance between the upper electrode and ground. The electrode gap is an additional parameter which can be varied to optimize the performance of these plasmas. In this study, performed on O@sub 2@/CF@sub 4@ chamber-cleaning plasmas in the capacitively-coupled Gaseous Electronics Conference Reference Cell, we investigated the correlations between electrode gap, electrical parameters, and the spatial distribution of the reactive CF@sub 2@ radical. Electrode gaps ranging from 0.5 cm to 2.25 cm were studied at pressures from 0.1 to 1.0 Torr. The 2-D density distribution of the reactive CF@sub 2@ radical was measured by planar laser-induced fluorescence (PLIF), and the regions where reactive species were generated were determined using spatially-resolved, broadband optical emission. The axial and radial uniformity and intensity of the emission and the CF@sub 2@ PLIF depended on both pressure and gap. The pressure at which the maximum radial uniformity in the CF@sub 2@ PLIF was observed correlated well with the maximum in I@sub ge@ but not with the minimum in plasma impedance. Measurements of rf current at the grounded electrode could be used to optimize the spatial distribution of reactive chemical species in reactors with differing electrode gaps, aiding in the optimization of chamber-cleaning plasmas and other fluorocarbon plasmas.

PS-MoP14 CF@sub x@ Radical and Etch Product Concentrations in Fluorocarbon Plasmas from Tunable Infrared Diode Laser Spectroscopy*, **Y. Men,*** University of Wisconsin, Madison, U.S.A*; I.C. Abraham, R.C. Woods,* University of Wisconsin, Madison

A sensitive diode laser spectrometer using multi-pass Herriot cells was employed in both an ECR etcher (30 passes with approximately 30 cm plasma depth) and in a 10 cm diameter, 1 m long hollow cathode DC discharge (46 passes). An IR diode laser operating near 1260 cm@super -1@ was used to study the CF@sub x@ (x = 1,2,3) radicals. Both CF and CF@sub 2@ were easily identified in a CF@sub 3@H ECR plasma, and their absolute concentrations were determined. Other fluorocarbon plasmas, e.g., C@sub 2@F@sub 6@ and C@sub 4@F@sub 8@, have also been investigated. The CF@sub x@ radical concentration dependences on plasma parameters, e.g., input power and neutral pressure, and on the partial pressure of added gases have been studied. To simulate actual etching conditions, radical concentrations over different wafer surfaces and at various bias powers have been measured. The CF@sub x@ concentrations with different reactant gases in the ECR etcher have been compared to those in the hollow cathode discharge. A diode laser operating in the 800-900 cm@super -1@ region is being used for similar investigations of SiF@sub x@ etch products.

PS-MoP15 Comparison of Plasma Density Measurements in ICP and Helicon Discharges using Langmuir probe, Plasma Oscillation Probe and Interferometry Techniques*, W. Zawalski,* Hiden Analytical Ltd.*; **J.D. Evans,*** University of California, Los Angeles

A comparison study of the application of various probe theories, including the so-called orbital motion limited@footnote 1@ and ABR@footnote 2@ theories, in the interpretation of Langmuir probe I-V characteristics is performed. Experimental data for the comparison is obtained in both an inductively coupled plasma (ICP) and a low-field helicon plasma source (HPS), over a wide range of parameters of interest to the plasma processing community.@footnote 3@ Measurements of N@sub e@ and N@sub i@ from the Hiden Electrostatic Plasma Probe (ESP) characteristics and ESPion software are compared to "known" values of N@sub e@ obtained via microwave interferometry and the plasma oscillation probe (POP) technique,@footnote 4,5@ in regimes including those where the probe theories yield different results. Closely spaced multiple peaks in the spectra of the POP are observed in some cases at higher RF input powers, possibly due to RF modulation of the source plasma density, leading to experimental uncertainty in N@sub e@ values thus obtained. Broadband low frequency electrostatic emissions and substantial peak broadening are observed when the beam-plasma instability excited by the probe is overdriven into the nonlinear regime. Other considerations for the applicability of the POP method will also be discussed. @FootnoteText@ @footnote 1@ J.G. Laframboise, Univ. Toronto Inst. Aerospace Studies Rept. 100 (1966). @footnote 2@ J.E. Allen, R.L.F. Boyd, and P. Reynolds, Proc. Phys. Soc. B 70, 297 (1957). @footnote 3@ N@sub p@ ~ 10@super 1@@super 0@-10@super 1@@super 2@ cm@super -@@super 3@, T@sub e@ ~ 2-4 eV, P@sub r@@sub f@ ~ 1 kW, P@sub o@ ~ 1-10 mTorr. @footnote 4@ T. Shirakawa and H. Sugai, Japan. J. Appl. Phys. 32, 5129 (1993). @footnote 5@ A. Schwabedissen et al., Plasma Sources Sci. Technol. 7, 119 (1998).

PS-MoP16 The Characteristics of PZT Thin Film by Dry Etching as a Variation of Substrate Temperature*, **T.H. An,** C.I. Kim, E.G. Chang,* Chung-Ang University, Korea

The Lead Zirconate Titanate PbZr@sub x@Ti@sub 1-x@O@sub 3@ (PZT) ferroelectric thin films have received a great attention for the application on nonvolatile memory, Infrared sensor, electro-optical device and microelectromechnical system device etc. In order to accomplish the integration of these device, the etching process for both PZT film and electrode material must be developed. In particular, much research of PZT ferroelectric films as a dielectric material for storage capacitors of highly integrated memory devices has been carried out since this films have a high dielectric constant and remanent polarization. However, there has been little study regarding the etching mechanisms of PZT material as a function of substrate temperature. Dry etching of PZT thin film was studied to examine the etching characteristics as a variations of substrate temperature. PZT films were deposited on Pt/Ti/SiO@sub 2@/Si substrates by sol-gel process. PZT thin films were etched with Cl@sub 2@/BCl@sub 3@/Ar gas combination in an inductively coupled plasma (ICP) by varying substrate temperature. Etching properties were investigated in terms of etch rate, etch selectivity, etch damage. To understand etching mechanism, Langmuir probe and Optical emission spectroscopy (OES) analysis were utilized for plasma diagnostic, also X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD) and secondary ion mass spectrometry (SIMS) analysis for film composition were utilized.

PS-MoP17 The Roles of N@sub 2@ Gas in Etching of Platinum by Inductively Coupled Ar/Cl@sub 2@/N@sub 2@ Plasmas*, **J.H. Ryu,** N.H. Kim, C.I. Kim, E.G. Chang,* Chung-Ang University, Korea

Recently, much efforts has been expected on etching of platinum film, which is the candidate of electrode material in the capacitor structure for future DRAM and ferroelectric RAM (FRAM). One of the most critical problem in etching of platinum was generally known that the etch slope was gradual. Therefore, the addition of N@sub 2@ gas to the Ar/Cl@sub 2@ gas mixture, which has been proposed the optimized etching gas combination for etching of platinum in our previous article,@footnote 1@, was performed. The selectivity of platinum film to oxide as an etch mask was increased with the addition of N@sub 2@ gas, and the steeper etch slope could be obtained. We interpreted these phenomena as the results of the blocking layer on the oxide mask shaped N-O and Si-N. And it was confirmed by TEM (transmission electron microscopy) and XPS (X-ray photoelectron spectroscopy) analysis. Moreover, it could be obtained the higher etch rate of platinum film. It was inspected that the more volatile compounds formed Pt-N were produced and the ion bombardment effects was increased. QMS (quadrupole mass spectrometry) and Langmuir probe were employed for each confirmation. @FootnoteText@ @footnote 1@ K. H. Kwon, C. I. Kim, S. J. Yun and G. Y. Yeom. "The Etching Properties of Pt Thin Films by Inductively Coupled Plasma", J. Vac. Sci. Technol. A 16(5), pp. 2772-2776, 1998.

**PS-MoP18 Neutral Depletion and Transport Mechanisms in Large-Area High Density Plasma Sources*, S.M. Yun*, *K. Taylor, G.R. Tynan,* University of California, San Diego

Plasma uniformity has been recognized as a significant parameter in large sized high density plasma processing tools. In this paper we show experimental and modeling results which indicate that significant neutral uniformity variations can also occur in high density plasma processing tools. The experiments are carried out in both inductively coupled plasma (ICP) and helicon plasma sources. The spatial distribution of reactive neutrals is measured using spatially resolved optical emission spectroscopy combined with Langmuir probe measurements of plasma density. The degree of on-axis neutral depletion is found to be determined by plasma density, neutral fill pressure, and neutral dissociation fraction. The observations can be explained by the "plasma pumping" effect, wherein electron impact ionization of neutral particles is followed by their rapid removal from the plasma by the presheath electric field. A one-dimensional neutral diffusion model that incorporates this mechanism provides reasonable agreement with our results. This net loss of neutral particles can result in a large (~50%) neutral density variation across 300mm wafers. The importance of neutral-surface interactions (i.e. the wall or wafer can be an effective source or sink of neutrals) is also examined.

PS-MoP19 The Study on The Method of Plasma-Generated-Polymer Attachment to PR Side Wall for Forming Smaller Contact Hole*, K.I. Seo,* *J.S. Hwang, U.I. Chung, K.W. Kang, M.-Y. Lee,* Samsung Electronic Co.Ltd., Korea

Resent PR (Photo Resist) patterning limit by KrF Deep UV (Ultra Violet) source is about 0.25~0.27µmm for contact pattern and 0.20~0.22µmm for line & space pattern. For patterning more small pattern size, line & space, new light sources such as ArF, X-ray, E-beam are being tested. But they are not adapted in mass fabrication yet. In this experiment, in order to overcome the patterning limit of photo process, we developed polymer attachment process to PR side wall for forming 0.15µmm size small contact. We tried to attach a uniform layer of polymer to PR side wall by generating various polymers in various gas plasmas such as CF@sub 4@/CHF@sub 3@/Ar, He/HBr, Cl@sub 2@/HBr. We found that C-Cl@sub x@-Br@sub y@ polymer, which has masking ability in the oxide etch process, was attached to PR side wall effectively in Cl@sub 2@/HBr gas plasma of the RIE (Reactive Ion Etching) type etcher which had a relatively high process pressure and a low density plasma. Based on the XPS (X-ray Photon Spectroscopy) result, the shape of the polymer attached PR, the dependency of the amount of the attached polymer on the contact size and the fact that polymer attachment process required PR loss, we proposed the mechanism of the polymer attachment process. It was observed the oxide etch rate was enhanced about 30% in contact hole size of 0.30µmm, and RIE-Lag was reduced in contact size range of 0.25~0.50µmm after the polymer attachment process, which needs further studies. We applied polymer attachment process to a real MDL (Merged DRAM with Logic) device, and obtained contact size of 0.15µmm by SEM (Scanning Electron Microscopy) measurement which was smaller than the contact size of normal process by approximately 50 nm as well as good size uniformity (@<=@ 20 nm), good particle (@<=@ 10 ea in entire wafer), uniform contact resistance in the range of 4800~5700@Ohm@/Cnt, and proper yield data.

PS-MoP20 Etching Mechanism of (Ba,Sr)TiO@sub 3@ Films in High Density Cl@sub 2@/BCl@sub 3@/Ar Plasma*, S.B. Kim,* Chung-Ang University, Korea*; Y.H. Lee,* Sung-Kyun-Kwan University, S.Korea, Korea*; G.Y. Yeom,* Sung-Kyun-Kwan University, Korea*; T.H. Kim,* Yeojoo Institute Technology, Korea*; K.H. Kwon,* Hanseo University, Korea*; C.I. Kim,* Chung-Ang University, Korea

(Ba,Sr)TiO@sub 3@ thin films have attracted great interest as new dielectric materials of capacitors for ultra-large-scale integrated dynamic random access memories (ULSI-DRAMs) such as 256 Mbit or 1 Gbit. In this study, Cl@sub 2@/BCl@sub 3@/Ar inductively coupled plasmas was used to etch (Ba,Sr)TiO@sub 3@ and the effect of etch parameter such as gas mixing ratio, coil rf power, dc bias voltage and chamber pressure. The characteristics of the plasmas were estimated using a Langmuir probe and optical emission spectroscopy (OES). (Ba,Sr)TiO@sub 3@ was etched under (Cl@sub 2@+BCl@sub 3@)/((Cl@sub 2@+BCl@sub 3@)+Ar) of 0.2. The maximum etch rate of the BST films was 56 nm/min under Cl@sub 2@/(Cl@sub 2@+Ar) of 0.2@super 1@, therefore Ar gas was constant at 0.2 and the ratio of Cl@sub 2@/BCl@sub 3@ was changed. The change of Cl, B radical density measured by OES as a function of BCl@sub 3@ percentage in Cl@sub 2@/BCl@sub 3@. The profile of (Ba,Sr)TiO@sub 3@ and residue remaining after the etch was investigated by scanning electron microscopy (SEM). To study on chemical reaction between BST and CF@sub 4@ and analysis composition of surface residue remaining after the etch, films etched with different Cl@sub 2@/BCl@sub 3@ gas mixing ratio were investigated using x-ray photoelectron spectroscopy (XPS) and secondary ion mass spectrometer (SIMS). @FootnoteText@ ACKNOWLEDGMENTS This work was supported by GRANT No. KOSEF 981-0908-032-2 from the Korea Science and Engineering Foundation. 1. S. B. Kim, C. I. Kim, E. G. Chang, G. Y. Yeom, "Study on surface reaction of (Ba,Sr)TiO@sub 3@ thin Films by high density plasma etching", J. Vac. Sci. Technol. A Jul/Aug. (1999) will be published.

PS-MoP21 Short Time Scale Instabilities of Ion Energies in an RF driven Fluorocarbon-Plasma*, G.J. Peter,* *N. Müller, H. Zogg, H. Oehre,* Balzers Instruments, Principality of Liechtenstein

Fluorocarbon gases are widely used for etching in the semiconductor manufacturing. Besides the desired etching, especially C@sub 4@F@sub 8@ tends to polymerisation and to a build-up of insulating coatings in the plasma chamber. The energy distributions of various ions from an RF-driven C@sub 4@F@sub 8@ -Plasma were investigated by a PPM (Plasma Process Monitor) to determine the influence of such coatings on the ion energy distribution. The PPM is a combination of a differentially pumped quadrupole mass filter and an energy analyser. An energy resolution of 0.3 eV and unit mass resolution over the whole mass range are achieved. The only part of the PPM exposed to the plasma is kept on floating potential so that coating here can not change the electrical potential. The maximum energy of the ions scattered out of the main discharge increased from initially 20 eV to 75 eV during the processing time of a single wafer (less than one minute). The energy rise was reproducible over several cycles. The initial energy was reached again after cleaning in a pure Argon plasma when a low content of C@sub 4@F@sub 8@ in Argon was used as sputter gas. So the effect can be attributed to the coating of the walls and electrodes. When pure C@sub 4@F@sub 8@ was used the coating was thus intense that it could not be removed by sputter cleaning any more. Electrical probes were tested to measure the shift of the plasma (sheet) potential, however they failed after a few minutes because they got coated. The results achieved show the usefulness of a mass spectrometer based plasma monitor whenever the ion energy is a critical process parameter. Applications are in basic plasma research as well as in pilot production plants.

PS-MoP22 Influence of Electode-size and Finite Rise Time Effects on Plasma Sheath Expansion*, G.-H. Kim,* Hanyang University, Korea*; H.-S. Uhm,* Ajou University, Korea*; S.-Y. Rhee, Y.-W. Kim,* Hanyang University, Korea*; S.-H. Han,* KIST, Korea*; M.-P. Hong,* Samsung Electronics, Korea

Influence of the electrode-size effects on plasma sheath expansion is investigated for a negative voltage (Vo) at the thin, flat, conducting, circular disk of radius (R). Properties of the ion sheath expansion in plasma are also investigated for a target voltage with a finite rise time. Results show that the sheath expansion is proportional to the square root of time at the beginning and is proportional to the five-sixth power of time later on. The propagation of the sheath front is proportional to the one-third power of the combination, 2VoR/pi. Experimental measurements have been carried out and the measured data are compared with the newly developed theoretical results. Those results agree remarkably well.

PS-MoP24 Diode Laser Spectroscopy of C@sub 2@F@sub 6@ Discharges in a GEC Reference Cell*, M.J. Barela,* *K.S. Waters, H.M. Anderson,* University of New Mexico

Diode laser absorption spectroscopy (DLAS), optical emission spectroscopy (OES) and Langmuir probe measurements were used to characterize an inductively coupled GEC Reference Cell as a function of reactor source power, bias power, pressure and heated silicon ring temperature while etching patterned oxide wafers. These measurements are used to construct response surface models of the tool's plasma chemistry behavior versus oxide and photoresist etch rate behavior. The oxide and photoresist etch rate behavior was found to also be profoundly influenced by the temperature of the cooling wafer chuck, so this became a fifth variable in the study. In a C@sub 2@F@sub 6@ discharge, CF and CF@sub 2@ radical concentrations measured by DLAS were also found to be highly dependent on wafer chuck temperature. In a 6 mTorr C@sub 2@F@sub 6@ discharge at 350 W source power and 75 W bias power, typical CF and CF@sub 2@

concentrations were in the range of 1x10@super12@ cm@super -3@ and 3x10@super 13@ cm@super -3@ range. However, if the wafer temperature is allowed to rise toward 100 C, the CF@sub 2@ concentration increases dramatically apparently due to greater photoresist interaction with the plasma. If the wafer is properly cooled, the oxide and photoresist etch rates appear to be dominated by bias power and at low bias power, net deposition of fluorocarbon polymer prevails over net etching. However, with increased wafer temperature, both power and bias exert a strong influence on film etch rates and etching occurs at even zero applied bias power. The data is expected to provide an important database for models of oxide etching in inductively coupled plasma tools. This project was funded by SEMATECH.

PS-MoP25 Silicon Oxidation-Depth Enhancement Employing Negative Ion under Transformer Coupled RF Bias*, **H. Shindo,*** Tokai University, Japan

Low temperature and low damage silicon oxidation technique is highly required in various ULSI processes. Especially for trench isolation of memory cell, the oxidation should be ion-assisted for directionality but with low damage. For this purpose, a method of negative ion assisted silicon oxidation was experimentally studied employing a microwave O2 plasma. A feasibility of high rate silicon oxidation with low damage at low temperature by negative ion was examined.In particular, effects of transformer coupled RF bias was deeply studied at various frequencies. The plasma produced in a 6 inch stainless-steel chamber was employed and the downstream plasma was mainly concerned because the negative ion was highly populated.Ion mass and energy analysis showed that the dominant negative ion was O- and its density was more than one order higher than O2-. The RF bias was applied with a transformer couple in combination with a DC voltage to irradiate the negative ion or positive one separately. The frequency of RF bias was varied from 40 kHz to 13.56 MHz. The oxidation depth showed a strong dependence on RF bias frequency, and its maximum was obtained at around 1 MHz, close to the negative ion plasma frequency.Thus it was concluded that the oxidation was due to the negative ions.The oxidation rate at the negative ion irradiation showed as high as 50 A/min at Vpp=65 V and it was five times higher than that at the positive ion irradiation of the same energy.This high rate of oxidation by the negative ion is due to its high chemical reactivity. An XPS analysis showed that in the film formed by the negative ion there was less suboxide compared with that by positive ion.

PS-MoP26 Deceleration of Silicon Etch Rate at High Aspect Ratios*, **J. Kiihamäki,*** VTT Electronics, Finland

The molecular flow conductance of a high aspect ratio feature can limit the etching species arriving at the bottom of the feature and thus limit the etch rate. Use of simple conductance model to predict etch rate of pulsed inductively couple plasma etch process gives good results when applied to linewidths typical in microelectromechanical systems (MEMS) at moderate aspect ratios, but at very high aspect ratio the conductance model does not predict the observed almost complete etch stopping. Other mechanisms are needed to explain it. In this paper the reasons of etch stop at the bottom of deep features are discussed. Measurement results of deep silicon etching are presented. Very deep holes of 30 and 60 µm diameter are etched into 1.3 mm thick silicon wafers to study the effect of process parameters. At moderate aspect ratios the bottom of the hole is nearly flat and side-walls are nearly vertical. At high aspect ratio the side-walls start to bow and the feature bottom turns into sharp spear head like. After long etch time the passivation breaks down near the top of the feature. The shape of the feature can have impact on step-coverage of passivation layer deposition during passivation step and passivation removal during etch step, which can cause the excessive sidewall etching and reduced etch rate at the feature bottom. Simple Monte Carlo calculation results of the effects of non-zero sidewall reaction probability and flow conductance of tapered tubes are presented. Main reason for etch stopping seem to be the loss of etchant species due to sidewall reactions.

PS-MoP28 Atomistic Simulations of Radical-Surface Interactions during Plasma-Enhanced Chemical Vapor Deposition of Si Films from Silane/Hydrogen Discharges*, S. Ramalingam, E.S. Aydil, **D. Maroudas,*** University of California, Santa Barbara*; S.P. Walch,* NASA Ames Research Center

Hydrogenated amorphous silicon (a-Si:H) films grown by deposition through silane-containing plasmas are widely used in solar cells and thin film transistors for flat panel displays. We present a study of the interactions of reactive radicals originating in the plasma with Si surfaces during plasma deposition from SiH@sub 4@/H@sub 2@ discharges based on recently developed classical force fields and ab initio calculations within density functional theory. Our simulation study employs a hierarchical approach that combines molecular-dynamics (MD) simulations for reaction identification and mechanistic understanding aided by molecular-statics and Monte Carlo simulations for reaction analysis. Interactions with isolated radicals during the initial stage of growth for each surface at submonolayer coverage are studied in detail to determine the surface chemical reactivity and the implications for the deposited film properties. The adsorption sites for the SiH@sub x@ (x=1,2,3) radicals are identified on the pristine and H-terminated Si(001)-(2X1) surfaces: the energetics of adsorption determined by the classical potential agree well with ab initio calculations. In addition, ultra-fast rate deposition of a-Si:H from each of the SiH@sub x@ radicals has been simulated through MD by repeatedly impinging the corresponding radical onto H-terminated Si(001)-(2X1) surfaces. SiH@sub 3@ radicals can abstract H atoms from the surface through an Eley-Rideal mechanism and return to the gas phase as silane molecules. Silyl radicals also can attach dissociatively onto the H-terminated Si surface at the dimer bond center. This insertion reaction leads to breaking of the dimer bond and subsequent transfer of a H atom from the radical to one of the dimer atoms resulting in the formation of two surface dihydride species. The energetics of this reaction is analyzed in detail both with classical and ab initio calculations. The theoretical results are compared with experimental observations.

PS-MoP29 Hydrogen Desorption from Acid Attacked Titanium after DC Glow-discharge Treatment*, **B.-O. Aronsson,*** University of Geneva, Switzerland*; B. Hjorvarsson,* Royal Institute of Technology, Sweden*; P. Descouts,* University of Geneva, Switzerland

Thermal desorption (TD) of hydrogen (H) from an acid attacked titanium (Ti) surface has previously@footnote 1@ been shown to depend on the presence of a surface oxide. The oxide was removed from Ti surfaces by using a DC glow-discharge (Ar plasma) treatment, and the subsequent change in the TD of absorbed H was studied. Biocompatibility is influenced by both surface chemical and topographical properties. In this study, the surface roughness of c.p. Ti samples was increased by at least a factor of 50 as measured by AFM.@footnote 1@ However, beside topographical modifications, acid attack also gives a dissolution of atomic H into the Ti sub-surface region and bulk which may result in a modification of the mechanical properties. Earlier work showed that TD above 400°C, where the oxide decomposes, is needed for H desorption.@footnote 1@ At these temperatures the morphology and mechanical properties of the Ti bulk are also modified and a lowering of the desorption temperature is desired. After plasma treatment the TD started below 300°C and the desorption activation energy was decreased from ca 2.0 (±0.3) to 0.8 (±0.2) eV/molecule. Ar plasma treatment was found to be efficient for a homogeneous sputter cleaning (characterized with AES), even of surfaces with a high surface roughness, and the native oxide was removed. The total amount of thermally desorbed hydrogen was inversely related to the plasma treatment intensity, while NRA profiles showed a complete elimination of the subsurface hydrogen after a medium intensity plasma treatment. AFM and SEM were used to characterize the topographical modification of plasma treated surfaces.@footnote 2@ @FootnoteText@ (1) Taborelli, M., et.al., Clinical Oral Implants Research, 1997, 8, 208-216 (2) Support from the ITI Foundation for the promotion of oral implantology, Switzerland, and from the Swiss National Fund, are greatly acknowledged.

PS-MoP31 Investigation of the TEOS Dissociation Coefficient by Electron Impact*, **C. Vallee**, A. Rhallabi, A. Granier, A. Goullet, G. Turban,* University of Nantes, France

Although O@sub 2@/tetraethoxysilane (TEOS) PECVD has been extensively used to deposit SiO@sub 2@-like films, the dissociation cross section of TEOS by electron impact is still unknown. In fact, most of the effort has been devoted to the determination of the TEOS fragmentation by O atoms (ko) since it is generally assumed that oxygen atoms are responsible for the dissociation of TEOS. Nevertheless, thanks to the experimental results obtained in a helicon reactor, it was suggested that TEOS fragmentation in a low pressure O@sub 2@/TEOS plasma was mainly achieved by electron impact while the main role of oxygen atoms was the etching of the organic part of the growing film. To get better insight into the TEOS dissociation by electron impact, we tried to determine the TEOS dissociation coefficient ke in a rf helicon reactor by developing a simple model which describes the experimental evolution of the growth rate with the distance from the TEOS injection. In this experiment, the TEOS gas is introduced at a point of the wall reactor instead of using a dispersal ring. A radial evolution of the deposition rate is obtained which can be related to a radial consumption of the TEOS. The model which gives ke at 3 eV (2 mTorr), is based on the following assumption: i) the deposition rate is proportional to the flux of fragments coming from the TEOS fragmentation by electron and oxygen atoms; ii) the spatial variation of the TEOS concentration is determined using a one-dimensional chemistry model. The first hypothesis requires the use of a sticking coefficient s. Dependence of ke with the value of s introduced in the model is also investigated. Finally, we found ke to vary from a few 10@super -8@ cm@super 3@s@super -1@ to a few 10@super -7@ cm@super 3@s@super -1@.

PS-MoP32 Electron Energy Control in Inductively Coupled Plasma Employing Multi-Mode Antenna*, H. Shindo,* ***T. Urayama,*** Tokai University, Japan

In the deep sub-micron etching for ultra large-scale-integrated circuit(ULSI) processes, numerous requirements of the plasma, such as high aspect ratio, high etching selectivity, are becoming increasingly critical. The requirements have promoted development of low-pressure and high density plasma. In these plasmas, however,the electron energy is prone to become too high at low pressures. In this work, a method of electron energy control was studied in an inductively coupled plasma by employing different azimuthal mode antenna. It is expected for electron energy to reduce at higher azimuthal mode antenna, because induction field is reversed with a shorter length. An inductively coupled plasma(ICP)was produced in a stainless-steel chamber of 350mm in diameter by supplying the RF power of l3.56MHz through the quartz window at one end. Langmuir probe diagnostics and optical emission spectroscopy were made through several vertical and horizontal ports of the chamber. The antenna is basically constructed with copper sheet of 0.3mm thickness, and the different azimuthal modes of m=0 and m=1 of one-loop antenna are realized by changing the feeder points of the RF current.The electron energy reduction was found in the m=1 mode by Langmuir probe measurement. This behavior was also confirmed by optical emission spectroscopy. The ArII lines became more intensive in the m=0 mode, while the ArI lines less intensive. The energy reduction in the m=0 mode was considered due to reverse of induction field with a shorter length in the higher mode antenna. The electron energy distribution function also showed less averaged energy in the m=1 mode.

PS-MoP33 Magnetized Inductively Coupled Plasma Etching of III-nitrides in Cl@sub 2@/BCl@sub 3@/O@sub 2@ and Cl@sub 2@/BCl@sub 3@/N@sub 2@*,* ***Y.H. Lee,*** SungKyunKwan University, Korea*; Y.J. Sung,* SungKyunKwan University, Korea, S.Korea*; G.Y. Yeom,* SungKyunKwan University, Korea*; J.W. Lee, T.I. Kim,* SAIT, Korea, South Korea

In this study, Cl@sub 2@/BCl@sub 3@/O@sub 2@ and Cl@sub 2@/BCl@sub 3@/N@sub 2@ inductively coupled plasmas were used to etch III-nitrides (GaN, AlN, and InN) and the effects of etch parameters such as gas combination and the effects of the magnets on the characteristics of the plasmas and etch properties of III-nitrides were investigated. The role of additive gases such as N@sub 2@ and O@sub 2@ to Cl@sub 2@/BCl@sub 3@ based plasmas to the etching of III-nitrides and the characteristics of plasma were estimated using a Langmuir probe, optical emission spectroscopy (OES), and quadrupole mass spectroscopy (QMS). Surface residue remaining after the etching was also investigated using x-ray photoelectron spectroscopy (XPS). The addition of O@sub 2@ and N@sub 2@ in Cl@sub 2@/BCl@sub 3@ generally increased III-nitrides etch rates for the small addition of O@sub 2@ and N@sub 2@ because more dissociated Cl radicals were generated by recombination processes (BO, B@sub 2@O, B@sub 2@O@sub 3@, and BN) between B from BCl@sub 3@ and O from O@sub 2@ or N from N@sub 2@. Using optical emission spectroscopy, radical peak intensities of BO, B@sub 2@O, B@sub 2@O@sub 3@, BN, and Cl intensity were estimated. The change of Cl radical density estimated by OES and QMS as a function of gas combination showed the same trend as the change of III-nitride etch rates, therefore, the etch rates of III-nitrides were related to the abundance of chlorine radical. Also, the use of magnets to the inductively coupled plasmas enhanced the etch rates of III-nitrides and improved the etch profile. We will show the effects of the magnets on the characteristics of the plasmas and the etch properties in more details at the presentation.

PS-MoP34 Grid Interactions with a High Density Plasma Source*,* ***J.E. Johannes,*** *T.J. Bartel,* Sandia National Laboratories*; C.K. Kim, D. Ecnomou,* University of Houston

Plasma interaction with a grid/screen is important in a number of applications. In neutral beam etching, for example, a grid is used to neutralize ions and generate collimated beams of energetic neutrals for anisotropic etch without charge damage. Neutron generators, used for neutron activation analysis in downhole logging, use a grid to define the Child-Langmuir surface where electrons are shielded, to extract an essentially pure ion beam for acceleration to a target. Finally, many ion sources and satellite thrusters are based on extraction of an ion beam from a plasma through a grid. The plasma conditions and the grid hole aspect ratio determine the neutral, ion, or plasma transport through the grid. Plasma-grid interactions are investigated for a range of plasma densities (1x1017-1x1019 #/m3) using particle based plasma simulation tools, and results are compared to experimental data. Icarus, a 2-D transient Direct Simulation Monte Carlo (DSMC) code and Mercury, a computationally fast, steady-state particle code are used to investigate the plasma behavior in front of and behind the grid. Electrons, ions and neutrals are treated as particles and an explicit Poisson solver, using the boundary element method, is used to compute electric fields. Simulations of both hydrogen and argon plasmas in an inductively coupled source were performed to generate boundary conditions for the grid. The grid hole diameter ranges from 30-1000 microns with a grid thickness of 250 microns. Simulation results are compared to measured ion fluxes and angular distributions collected over a range of grid hole aspect ratios. The optimal interaction parameters and hole aspect ratio required to minimize ion escape through the grid for neutral beam applications are discussed. Plasma-grid interaction calculations were also performed for higher density plasmas (1x1019 #/m3) typical of an arc discharge to investigate optimized hole aspect ratios for ion extraction for neutron generator applications.

PS-MoP35 Ultra-shallow n+/p and p+/n Junctions formed by Plasma Immersion Ion Implantation*,* ***J.D. Bernstein,*** *P.L. Kellerman, W. Krull, Yu. Erokhin, P. Frisella,* Eaton Corp.*; M.J. Rendon,* Motorola APRDL/Sematech

Plasma immersion ion implantation (PIII) is an emerging method being developed for shallow junction formation and other low energy, high dose ion implantation applications. The PIII process consists of placing a Si wafer in a plasma containing a desired dopant species and pulse-biasing the wafer to negative potentials in order to accelerate and implant dopant ions. In this work, BF@sub 3@, PH@sub 3@, and AsH@sub 3@ PIII are used for formation of ultra-shallow n+/p and p+/n junctions. As-implanted boron profiles produced from 2 to 10 kV BF@sub 3@ PIII are compared to those from mass-analyzed BF@sub 2@ implantation. The differences in the dopant profiles are attributed to the PIII ion energy distribution and the BF@sub 3@ plasma species composition. The relationship between sheet resistance and junction depth is investigated for PIII and mass-analyzed implants processed with a 1050 @super o@C spike anneal. Both n+/p and p+/n junctions produced by PIII meet S/D junction requirements of the National Technology Roadmap for Semiconductors (NTRS) for 70 nm CMOS devices.

Thin Films Division

Room 4C - Session TF-MoP

Poster Session

TF-MoP1 Effect of HCl Catalyst in the Formation of Flat Structures of Ta@sub 2@O@sub 5@ Thin Films by Sol-Gel Technique*, S. Santucci,* ***C. Cantalini,*** *A.R. Phani,* University of L'Aquila, Italy

Stoichiometric Ta@sub 2@O@sub 5@ thin films have been successfully deposited on Si (100) substrates by sol-gel technique using tantalum ethoxide as precursor. The films were annealed at different temperatures. The compositional and structural characteristics of the films were systematically examined with the aid of X-Ray Diffraction, Atomic Force Microscopy and X-ray Photoelectron spectroscopy. We demonstrate that upon using Hydrogen chloride (HCl) as catalyst, we obtained uniform flat like structures of Ta@sub 2@O@sub 5@ as observed in tapping mode atomic force microscopy, when compared to the samples without it. X-ray Photoelectron spectroscopy measurements have shown the small presence of SiO@sub 2@ interface layer in the deposited films. A plausible mechanism to obtain flat structures is also explained.

TF-MoP2 Mechanical Properties and Residual Stresses in AlN Films Prepared by Ion Beam Assisted Deposition*,* ***Y. Watanabe,*** *N. Kitazawa, Y. Nakamura,* National Defense Academy, Japan*; C. Li, T. Sekino, K. Niihara,* Osaka University, Japan

Aluminum nitride (AlN) thin films were prepared on silicon single crystal substrates by ion-beam assisted deposition method, and the influence of the nitrogen ion beam energy on mechanical properties and residual stresses was studied by changing the nitrogen ion beam energy from 0.1 to 1.5 keV. Mechanical properties were examined by a nano-indentation method and residual stresses were evaluated by film curvature measured by an optical cantilever system. The films show elastic behaviors during loading and unloading processes, but the residual depth after the unloading process increases with increasing the ion beam energy, resulting in decreasing in the returned energy ratio. All the films are found to be in compressive stress state and the values of the stress decrease with increasing the ion beam energy. Decreasing tendency is also observed in the relationship between the ion beam energy and film hardness. So as to study the effect of thermal treatment on relaxation of residual stresses, the films were annealed in nitrogen atmosphere at 723 K, and it is found that the films prepared with the high energy ion beam are relaxed more easily than those prepared with the low energy ion beam. These results suggest that rearrangement of AlN occurs readily in the films prepared with the high energy ion beam. It is proposed that the mechanical properties and residual stresses are closely related with each other and they can be controlled by the ion beam energy.

TF-MoP3 The Effects of Temperature and Morphology on the Electron Stimulated Desorption of H@super -@ from Thin Hydrocarbon Films*, **A.D. Bass**, L. Parenteau, F. Weik, L. Sanche,* University of Sherbrooke, Canada

In recent years, low energy electron impact techniques have been used to study thin molecular solids under ultra high vacuum (UHV) and have provided valuable information on the electronic interactions that underlie such phenomena as radiation damage to biological materials, dielectric aging and surface mediated photo-chemistry.@footnote 1@ Measurements of the electron stimulated desorption (ESD) of molecular and atomic anions have in part revealed the importance in radiation damage of such processes as dissociative electron attachment (DEA) and dipolar dissociation (DD). In general, the molecular films used in these studies are formed by vapor deposition under UHV conditions. Until very recently,@footnote 2@,@footnote 3@ little consideration was given as to how film preparation and morphology affected ESD measurements and we address questions of this type in this work. We present measurements of the ESD yield of H@super -@ from pure films of n-hexane, ethyl-benzene and benzene as a function of incident electron energy (0 - 20 eV) at various film temperatures between 20 K and their respective sublimation points. The three molecules were chosen as their films display contrasting degrees of porosity, crystallinity etc., Our measurements reveal the variation in the ESD yield from DEA and DD processes as a function of film temperature (and hence morphology). These changes are correlated to others seen in the low energy electron transmission spectra for films of the same molecules deposited at various temperatures. @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 and l. Sanche, J. Chem. Phys. 107 8668 (1997) @footnote 3@K.P. Stevenson, G.A. Kimmel, Z. Dohnalek, R.S. Smith and B.D. Kay, Science 283 1505 (1999).

TF-MoP4 Oxidation Studies and Chemical State Analysis of Polycrystalline Magnetron Sputtered (Ti,Al)N Films*, **A. Kale**, S. Seal, S. Sundaram,* University of Central Florida

In order to improve the functional properties of hard coatings, recent investigations have been directed to Ti-N based multicomponent materials. In particular the nitride (Ti,Al)N with a Ti:Al ratio of 1:1 seems to be a promising alternative to the widely used TiN. A disadvantage of TiN in high-temperature applications is that it oxidizes rapidly at temperatures above 500 C. In contrast, (Ti,Al)N coatings are characterized not only by high microhardness and dense microstructure, but also by much higher thermal stability. They exhibit better oxidation resistance and hence improved performance over that of TiN. Because of their outstanding properties with respect to hardness, wear resistance, oxidation resistance and corrosion resistance, it seems to be desirable to study the crystal structure and mechanical and chemical properties in detail. The (Ti,Al)N coatings were dc sputter deposited onto 316SS substrates under ambient as well as liquid nitrogen temperatures. The as formed films were oxidized in a vertical fused-silica tube furnace in a pure O2 flowing atmosphere at varying temperatures (700-900C). Both types of films were compared to each other with respect to their mechanical as well as chemical properties. The characterization work involved x-ray diffraction (XRD) to study the amorphous or crystalline nature of the films thus predicting their crystal structure. Scanning electron microscope (SEM) and transmission electron microscope (TEM) images will provide information about the particle size and film thickness. Auger electron spectroscopy (AES) and x-ray photoelectron spectroscopy (XPS) will provide rapid information of elements in the top few atomic layers in addition to the compositional analysis and detailed chemical bonding information. The difference in film stoichiometry will be compared at the two different deposition conditions and will thus reflect their behavior under oxidizing conditions.

TF-MoP5 Characterization of VO@sub 2@ Epitaxial Films with Different Orientations Grown on Sapphire (110) by Sputtering*, **P. Jin**, S. Tanemura,* National Industrial Research Institute of Nagoya, Japan*; K. Macak, U. Helmersson,* Linkoping University, Sweden

Vanadium dioxide is one of the most important compounds in the V-O system. It exhibits a semiconductor-to-metal phase transition at 68°C, accompanied by large changes in electrical resistivity (up to 10@super 5@) and optical properties (from transmitting to reflecting in the infrared). Thin films of vanadium dioxide have been studied for electrical and optical switching devices. It is known that an epitaxial film, which can be grown on sapphire substrate, exhibits properties comparable to single crystal. However, there is little information on the deliberate control of orientation of an epitaxial film and the effect on film property. In this study, thin films vanadium dioxide were grown using DC reactive magnetron sputtering on single crystal 110-oriented sapphire substrates held at 400-600°C. The magnetron source was of the unbalanced type giving rise to more intense bombardment as compared to conventional sources. Different film orientations was achieved with different sputtering geometry, most likely due to varying energetic particle bombardment and growth rate, i.e., an on-axis deposition (substrate facing target) and an off-axis deposition resulted in well-defined (100)- and (001)- oriented epitaxial films, respectively. The epitaxial films were examined by x-ray diffraction using conventional @theta@-2@theta@ scans, rocking curves, and pole figure plots. The compositions were determined from Rutherford backscattering spectroscopy (RBS) and the surface morphologies were studied with atomic force microscopy (AFM). The different film orientations resulted in significant difference in film properties such as the temperature and sharpness of the phase transition, as confirmed from the measurement of electrical resistance vs temperature.

TF-MoP6 Towards a Fully Monitored Fourier Transform Infrared Spectroscopic Ellipsometer*, **J.C. Cigal**, G.M.W. Kroesen,* Eindhoven University of Technology, The Netherlands

Infrared ellipsometry emerged few years ago as a powerful sensitive and non-intrusive optical technique for characterizing of surfaces, interfaces and thin films. The recent improvements in Fourier transform analysis and of polarizers helped to overcome problems formerly restricting the applications of such a technique. Among the different ellipsometer configurations in use, we opted for a rotating compensator ellipsometer running in the middle infrared. This technique offers several advantages compared to other ellipsometric methods, such as the non-ambiguous determination of ellipsometric parameters and the insensitivity to source and detector polarization. However, the principal fact preventing a widespread application of rotating compensator for spectroscopic purposes was the absence of a good spectroscopic retarder. We are currently developing one available in the 1000-4000 cm@super -1@ spectral range. The principle is based on internal reflection inside a Zinc Selenide crystal. Moreover, measurement speed can significantly be improved by an accurate synchronization between the scanner of the spectrometer and the stepping motors used to rotate the polarizers and the compensator. This will allow us, as a next stage, to perform in-situ and real time measurements.

TF-MoP7 Improved Light Stability of Colored SiO@sub 2@ Coatings Containing Organic and Metalorganic Dye Molecules*, L.L. Diaz-Flores,* Inst. Tecnologico de Saltillo, Mexico*; J.J. Perez-Bueno,* Univ. Autonoma de Queretaro, Mexico*; F.J. Espinoza-Beltran, R. Ramirez-Bon, **Y.V. Vorobiev**, J. Gonzalez-Hernandez,* CINVESTAV-IPN, Mexico

The sol-gel method has been used to prepare SiO@sub 2@coatings containing various amounts of organic and metalorganic dyes, introduced in the starting solutions. The starting solutions were mixed of tetraethylorthosilicate, water and ethanol. In order to have a better dispersion of the molecular dye into the glass matrix, the starting solutions were subjected to a milling process at various times using an appropriated ball mill. It is observed that in the coatings prepared from solutions without the milling process, the dye is agglomerated into small particles and those prepared from solutions subjected to the milling process show much better dye dispersion. A good dispersion is achieved after about 4 hr of milling, this is reflected in an increase in the optical absorption and makes the samples stable to light exposure. Both results are explained using a model which predicts the degree of dye dispersion. Using this model, an estimation of the size of the dye aggregates is made.

TF-MoP8 Diamond Formation Using a Low-Pressure Inductively Coupled Plasma, ***H. Ito,*** Nagoya Municipal Industrial Research Institute, Japan; *K. Teii,* Nagoya University, Japan; *M. Ito,* Wakayama University, Japan; *M. Hori,* Nagoya University, Japan; *T. Takeo,* Nagoya Municipal Industrial Research Institute, Japan; *T. Goto,* Nagoya University, Japan

Diamond was successfully synthesized by using a H@sub 2@-rich CH@sub 4@/CO/H@sub 2@ and H@sub 2@-rich CH@sub 4@/H@sub 2@ inductively coupled plasma at a low pressure of 11 Pa. The ratio of particle size to deposition time, which is a criterion of the diamond growth rate, in H@sub 2@-rich CH@sub 4@/CO/H@sub 2@ mixture gas plasmas was larger than that in H@sub 2@-rich CH@sub 4@/H@sub 2@ mixture gas plasmas. The nondiamond phases in the deposits increased as CO gas was added to H@sub 2@-rich CH@sub 4@/H@sub 2@ mixture gas as observed by the Raman spectra. In order to investigate the mechanism for the diamond formation, C-atom densities in the plasmas were measured by using a vacuum ultraviolet absorption spectroscopy. In addition CH, OH, H-atom emission intensities were measured by optical emission spectroscopy. As a result, the C-atom densities and OH emission intensity increased with increasing the mixture ratio of CO to CH@sub 4@, while CH and H-atom emission intensities were almost constant. The generation of C-atoms from CO gases was much larger than that from CH@sub 4@. On the basis of the correlation between the quality of deposits and the C-atom densities in the plasma, C-atoms were found to contribute to form amorphous carbon phases rather than diamond phase. Moreover, using the low-pressure inductively coupled diamond formation plasmas, the importance of the abstraction of diamond surface-bonded H-atoms by OH radicals was suggested.

TF-MoP9 Microstructure of Ti:D Films Prepared by Reactively rf Sputtering, ***S. Nakao,*** *P. Jin, K Saitoh, Y. Miyagawa, S. Miyagawa,* National Industrial Research Institute of Nagoya, Japan

Metal deuteride films have attracted much attention because of potential application for neutron source in ion beam technology. Especially, titanium deuteride (Ti:D) films are much stable at relatively high temperature up to about 400 @super o@C. In this study, Ti:D films were prepared by reactively rf sputtering and the microstructure was examined. Ti:D films were deposited mainly on Si substrates under the various conditions of the rf power and the ratio of Ar and D@sub 2@ gases. Thin film x-ray diffraction (XRD) measurements were carried out to examine the crystal structure of the films. Rutherford backscattering spectrometry (RBS) and elastic recoil detection analysis (ERDA) were performed with a 1.7 MV tandem-type ion accelerator to analyze the composition of the films. From the results of the XRD measurements, it was found that the Ti:D films have a delta-phase (fluorite) crystal structure at low rf power of 100 W. However, the results of RBS and ERDA measurements revealed that the Ti:D films contained the impurity elements such as hydrogen and oxygen. It was inferred from the quantitative analysis that the films were composed of delta-phase titanium deuterides (or hydrides) and amorphous titanium oxides.

TF-MoP10 Growth of Si Thin Films on CeO@sub 2@/Si(111) Substrate Prepared by Electron Beam Evaporation, ***C.G. Kim,*** *J.H. Yang, B.S. Moon, C.Y. Park,* Sung Kyun Kwan University, Korea

The Si/CeO@sub 2@/Si structure is one of the silicon-on-insulator (SOI) and was prepared by a hetero-epitaxially growing method. Cerium dioxide(CeO@sub 2@) is an insulating material with a lattice mismatch of 0.35% to silicon. Si film was grown on CeO@sub 2@(111)/Si(111) substrate by using high-vacuum evaporation. We have studied on the growth mechanism of Si for the various deposition conditions and analyzed by X-ray diffraction, double crystal XRD, TEM, AFM and the mobility measurement. For homo-epitaxial growth of Si, a better epitaxial Si film had been formed 800@super o@C. But, for the Si epitaxial growth on the CeO@sub 2@(111)/Si(111) the substrate temperature was limited to about 620@super o@, because a dissociated oxygen from CeO@sub 2@ and an out-diffused carbon. The Si film was epitaxially growth along (111) direction of the CeO@sub 2@ at 620@super o@C and consisted of domains oriented along (111) direction. The mobility was 56.4cm@super 2@/(Vs) at carrier density of 5.87x10@super 19@/cm@super 3@.

TF-MoP11 Origin of Electrical Property Distribution on Surface of ZnO:Al Films Prepared by Magnetron Sputtering, ***T. Minami,*** *T. Miyata, T. Yamamoto, T. Nishitani,* Kanazawa Institute of Technology, Japan

This paper investigates the origin of electrical property distribution on the substrate surface of ZnO:Al films prepared by magnetron sputtering on substrates placed parallel to the target surface. The films were prepared using a magnetron sputtering apparatus with a sintered or powder target (diameter of 140mm) and either a dc or rf plasma power source. When the films were prepared on substrates at the same temperature with the same deposition rate under optimized sputter deposition and target preparation conditions, the lowest obtained resistivity found in ZnO:Al films prepared by either dc or rf magnetron sputtering was roughly the same. However, the ZnO:Al films prepared by dc sputtering exhibited a larger increase of resistivity at locations on the substrate corresponding to the target erosion area than found in films prepared by rf sputtering. In contrast, the resistivity distribution of ZnO:Al films prepared by rf magnetron sputtering with an applied external magnetic field which focused the rf plasma was similar to that of films prepared by dc magnetron sputtering. Thus, the difference in electrical property distribution obtained between rf and dc magnetron sputtering is mainly related to the activity and amount of oxygen reaching the substrate surface as well as its spatial distribution.

TF-MoP12 Effect of C@sub 2@ Radicals on Diamond Growth Using Low-Pressure, Radio Frequency, CH@sub 3@OH/H@sub 2@/H@sub 2@O Inductively Coupled Plasma, ***T. Shiomi,*** *H. Nagai, M. Hiramatsu, M. Nawata,* Meijo University, Japan

Previously we demonstrated the successful formation of diamond crystals using a low-pressure, radio frequency (rf, 13.56 MHz), inductively coupled plasma (ICP) in the total pressure range of 9.3-18.6 Pa.@footnote 1@ In contrast with conventional methods of diamond chemical vapor deposition (CVD) employing high-pressure plasma (@>=@100 Pa), in the case of low-pressure, high-density, and highly dissociated plasmas, carbon dimer (C@sub 2@) radicals or carbon atoms instead of methyl radicals might be major species for film formation. C@sub 2@ radical is considered to be one of important radicals for the nanocrystalline diamond deposition using plasma-enhanced CVD.@footnote 2@ In this work, C@sub 2@ radical density in a low-pressure (@<=@13 Pa), rf-ICP employing CH@sub 3@OH/H@sub 2@/H@sub 2@O source for diamond CVD was measured using absorption spectroscopy with Xe lamp emitting a continuous spectrum as a light source. The correlation between the absolute C@sub 2@ radical density and the quality of diamond films was investigated. In the Raman spectra of diamond formed using a low-pressure rf-ICP, a broad peak around 1140 cm@super -1@ arising from nanocrystalline diamond was observed together with the strong 1332 cm@super -1@ diamond Raman peak. C@sub 2@ radical density increased almost linearly with increasing rf input power or CH@sub 3@OH partial pressure. On the other hand, C@sub 2@ radical density decreased with increasing H@sub 2@O partial pressure, while the intensity of 1332 cm@super -1@ diamond Raman peak increased with increase of the H@sub 2@O partial pressure up to 5.3 Pa. @FootnoteText@@footnote 1@H. Noda, H. Nagai, M. Shimakura, M. Hiramatsu, and M. Nawata, J. Vac. Sci. Technol. A 16, 3170 (1998). @footnote 2@D. M. Gruen, S. Liu, A. K. Krauss, and X. Oan, J. Appl. Phys. 75, 1758 (1994).

TF-MoP13 Properties of Indium Oxide Thin Films Prepared by Reactive Electron Beam Evaporation Technique for EMI Control, ***J. Asbalter,*** *A. Subrahmanyam,* Indian Institute of Technology, India

It is well known that transparent conductors like Indium oxide (IO) are good Electro Magnetic Interference (EMI) shields. In the present investigation, the EMI shielding property of indium oxide thin films has been studied as a function of growth temperature. All the IO films are grown on glass substrates by reactive electron beam evaporation technique at a chamber pressure (with the reactive gas, oxygen) of 2.5 x 10@super -4@ milli bar. The substrate temperature is varied between 160@super o@C - 200@super o@C. All the films show metallic properties (carrier concentration, N = 10@super 19@/cc, Hall Mobility =20-30 cm@super 2@ V@super -1@ sec@super -1@) with an optical transmission above 85% (at 500 nm wavelength). It is found that the EMI shielding efficiency (SE) of IO films (of 100 nm thickness) is very much comparable to that of the silver coated metal sheet in the measured frequency range 1 MHz till 100 MHz . As is well known that high frequecny shielding is related to the plasma frequency and the low frequency shielding is dependant on the magnetic properties. The AC (magnetic) susceptibility of the films measured in the temperature range 300 K till 6 K show very interesting magnetic properties. All the films show diamagnetic behavior at room temperature (300 K). For the films prepared at 200@super o@C, there is a clear paramagnetic behavior below 250 K. Present work analyses the reasons for the paramagnetic nature and its consequence on the low frequency (< 10 MHz) shielding efficiency.

TF-MoP14 Diffusion of Cu from PVD Al-Cu Alloy and CVD Cu Thin Films into CVD Al Thin Films Inside Submicron Via Holes*, **B. Rogers,*** Vanderbilt University

Solid state diffusion of Cu from copper containing films into a chemical vapor deposited (CVD) Al film was evaluated as a method to dope the CVD Al with Cu atoms to enhance its electromigration resistance. CVD Cu and PVD Al-1.5 wt% Cu thin films were used as the copper sources. Thin film stacks consisting of CVD Al/CVD Cu and PVD Al-Cu/CVD Al were deposited onto unpatterned silicon dioxide films as well as silicon dioxide films patterned with 0.6-micron diameter by 1.2-micron deep via holes. Samples were annealed for 0, 5, 15, or 60 minutes at 360, 390, or 420 degrees Celsius. Backscatter electron microscopy was used to image theta phase (Al@sub 2@Cu) precipitates inside vias. The number of precipitates and fraction of via cross-sectional area covered by the precipitates were used to estimate the amount of Cu present in the vias. These results are compared to Rutherford backscatter spectrometry and Auger electron depth profiling analyses of samples with films deposited onto unpatterned substrates.

TF-MoP15 Process Control and Properties of Aluminum Doped Zinc Oxide Films Deposited by High Rate Mid-frequency Reactive Magnetron Sputtering*, **N. Malkomes,** M. Vergöhl, B. Szyszka, T. Matthée,* Fraunhofer Institute for Surface Engineering and Thin Films, Germany

Aluminum doped Zinc oxide films are promising candidates for economic TCO applications. To reach high deposition rates (about 7 nm/s at 4.5 W/cm2) in combination with optimum TCO properties by reactive mid-frequency (MF) sputter technique, the process window has to be precisely controlled. In order to overcome the typical hysteresis problem the process stabilization was done by plasma impedance control for ease of use, enabling to stabilize the deposition process in any working point on the s-curve of the corresponding hysteresis loop. In addition the setpoints were characterized by partial pressure measurements, optical emission spectroscopy (OES), and with in-situ spectroscopic ellipsometry. The influence of deposition parameters (working point, pressure, temperature) on the electrical and optical properties as well as film growth and morphology were studied by photometry, Hall-measurements and in-situ and ex-situ spectroellipsometry, respectively. Due to the bandgap widening the optimum films show neutral color. The ellipsometric spectra could be well modelled without using interface layers indicating the dense structure of the films. Electrical measurement yield that the optimum resistivity of ZnO:Al films deposited on unheated substrates is about 2.5 times higher than at 200Â°C substrate temperature. In the latter case, a value of 290ÂµOhm cm could be reached. In addition the process window of stoichiometric films is widened due to oxygen partial pressure limited forming of the film on the heated substrate. .

TF-MoP16 Low-temperature Growth of Ti(C,N) Thin Films on D2 Steel and Si(100) Substrates by PEMOCVD*, B.-C. Kang, J.-H. Boo, Y.K. Cho, J.-G. Han, **C.H. Heo,*** SungKyunKwan University, Korea

We have deposited Ti(C,N) thin films on Si(100) and D2 steel substrates in the temperature range of 150 - 300 @super o@C using tetrakis diethylamido titanium (TDEAT) and titanium isopropoxide (TIP) by pulsed DC plasma enhanced metal-organic chemical vapor deposition (PEMOCVD) method. Polycrystalline Ti(C,N) thin films were successfully grown on either D2 steel or Si(100) surfaces at temperature as low as 150 @super o@C. Compositions of the as-grown films were determined with XPS and RBS. From XPS analysis, thin films of Ti(C,N) with low oxygen concentration were obtained. RBS data were also confirmed the changes of stoichiometry and microhardness of our films. Radical formation and ionization behaviors in plasma are analyzed by optical emission spectroscopy (OES) at various pulsed bias and gases conditions. H@sub 2@ and He+H@sub 2@ gases are used as carrier gases to compare plasma parameter and the effect of N@sub 2@ and NH@sub 3@ gases as reactive gas is also evaluated in reduction of C content of the films. In this study, we found that He and H@sub 2@ mixture gas is very effective in enhancing ionization of radicals, especially N@sub 2@ resulting is high hardness. The higher hardness of film is obtained to be ca. 1700 HK 0.01 but it depends on gas species and bias voltage. The proper process is evident for H@sub 2@ and N@sub 2@ gas atmosphere and bias voltage of 600 V. However, NH@sub 3@ gas highly reduces formation of CN radical, thereby decreasing C content of Ti(C,N) thin films in a great deal. Compared to PVD TiN films, the Ti(C,N) film grown by PEMOCVD has very good conformability; the step coverage exceeds 85% with an aspect ratio of more than 3.

TF-MoP17 A Study on the Characteristics of TiN Thin Film Deposited by Atomic Layer Chemical Vapor Deposition Method*, **H. Jeon,** J.W. Lee, J.H. Koo, Y.S. Kim, Y.D. Kim, D.S. Kim,* Hanyang University, Korea

A TiN film which exhibits a NaCl structure is now used as a diffusion barrier in ULSI device because it shows a very low resistivity, good adhesion characteristics and thermal stability.@footnote 1@ In this study, we deposited TiN film on Si substrate by using atomic layer chemical vapor deposition system.@footnote 2@ The TiN film deposited by this method is expected to have excellent physical and electrical properties.@footnote 3@ In this system, the TiCl@sub 4@ and NH@sub 3@ gases as Ti source and an reactant were supplied, separately and Ar purge gas was added between each source and reactant supply to suppress the direct reaction between source and reactant. The process parameters to grow TiN were process temperature, number of cycle to supply the reactant and source gases, source supplying time, and purging time. After growing this TiN film, the physical and electrical properties were measured by XRD, AFM, SEM, AES, TEM, RBS and a four point probe. The crystallinity and the surface and interface were analyzed by XRD, SEM and TEM. The root mean square toughness of TiN surface was measured by AFM and its value was about 15Å. The chemical analysis was done by AES and the Cl content in TiN film was below the detection limit of Auger Electron Spectroscopy which was below 1%. We will compare these TiN thin film data with other deposition method, such as PECVD and MOCVD and will discuss the TiN film growing method based on the thermodynamic consideration and atomic size computer modeling. @FootnoteText@ @footnote 1@J. E. Sundgren, Thin Solid Films, 128, 21-44 (1985) @footnote 2@S. Yokoyama, H. Goto, T. Miyamoto, N. Ikeda, K. Shibahara, Applied Surface Science, 112, 75-81 (1997) @footnote 3@T. Suntola, Thin Solid Films, 216, 84-89 (1992).

TF-MoP18 Non-Stoichiometric PMN-PT Films Grown by Laser Ablation*, A. Fundora,* Universidad de la Habana, Cuba*; **J.M. Siqueiros,*** UNAM, Mexico*; J. Portelles,* Universidad de la Habana, Cuba

Films of Pb(Mg@sub 1/3@Nb@sub2/3@)@sub2.1@ Ti@sub0.3O3@ (PMN-PT) have been grown on Pt/SiO@sub2@/Si substrates by pulsed laser ablation. The dielectric and microstructural properties of the non stoichiometric thin films of the type: 2.1PMN-0.3PT are studied in this work. 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. Surface structure and cross section studies were performed by scanning electron microscopy (SEM). Curves of dielectric permittivity as a function of temperature and hysteresis loops are reported.

TF-MoP19 The Advancing Techniques and Sputtering Effects of Oxide Films Fabricated by Stationary Plasma Thruster with Argon and Oxygen Gases*, **J. Cho,*** KIST, Korea*; Y. Ermakov,* Mirea, Russia*; K.H. Yoon,* Yonsei University, Korea*; S.K. Koh,* KIST, Korea

The using of stationary plasma thruster (SPT) ion source, invented previously for space application in Russia , in experiments with surface modifications and film deposition systems is reported here. Plasma in the SPT is formed and accelerated in electric discharge taking place in the crossed axial electric and radial magnetic fields. Brief description of the construction of specific model of SPT used in the experiments is presented. With gas flow rate 39 ml/min, ion current distributions at several distances from the source are obtained. These was equal 1-3 mA/cm2 within an ion-beam ejection angle of ï‚± 20o with discharge voltage 160 V, for Ar as a working gas. Such an extremely high ion current density allows us to obtain the â€¦ films with deposition rate â€¦ by sputtering â€¦ target. It is shown a possibility of using of reactive gases in SPT (O2 and N2) along with high purity inert gases used for cathode to prevent the latter contamination. It is shown the SPT can be operated at the discharge and accelerating voltages up to 600 V. The results of presented experiments show high promises of the SPT in sputtering and surface modification systems for deposition of oxide thin films on Si or polymer substrates for semiconductor devices, optical coatings and metal corrosion barrier layers. Also, we have been tried to establish in application of the modeling expertise gained in electric and ionic propulsion to permit numerical simulation of additional processing systems. In this mechanism, it will be compared with conventional DC sputtering for film microstructure, chemical composition and crystallographic considerations.

TF-MoP20 An Alternative Procedure for the Deposition of Close-Spaced Sublimation CdTe/CdS Solar Cells*, **H.R. Moutinho,** R.G. Dhere, M.M. Al-Jassim, C. Ballif, L.L. Kazmerski,* National Renewable Energy Laboratory

In previous work (JVST 1998 and 1999), we demonstrated that a recrystallization process causes the changes in physical properties of CdTe films heat-treated with CdCl@sub 2@. Using this information, we were able to induce recrystallization in close-spaced sublimation (CSS) CdTe films, depositing these films at temperatures about 200°C lower than usually used in this process. This lower-temperature deposition process is very attractive in the fabrication of solar cells because it implies in energy economy, and also avoids or minimizes the problem with diffusion of impurities from the glass substrate to the active elements in the cell. In the present work, we deposited CSS CdTe films on solar-cell substrate structures using relatively low temperatures and varied deposition parameters, (e.g., deposition temperature and growth rate). We also subjected the films to two different treatments (dipping in CdCl@sub 2@/methanol solution and exposure to CdCl@sub 2@ vapor), and varied many parameters, such as treatment temperature and time, and saturation of the solution. The objective was to optimize the deposition and heat-treatment parameters to obtain high efficiency cells. The structure of the CdTe films was studied using atomic force microscopy, to obtain information on average grain size and surface topography; X-rays diffraction, to obtain information on lattice parameter and phase formation; and X-ray Photoelectron Spectroscopy, to study film composition. We correlated the various deposition and treatment parameters with the performance parameters (quantum efficiency, open-circuit voltage, short-circuit current, fill factor, and efficiency) of completed devices. We showed that, although the solar cells fabricated at higher temperatures still provide the best efficiencies, the low temperature method can produce solar cells with intermediate efficiencies (>10%), which will be more attractive for industrial application, because of the manufacturing and economic advantages.

TF-MoP21 CdS/CdTe Interface Analysis by Transmission Electron Microscopy*, **R.G. Dhere**, M.M. Al-Jassim, K.M. Jones, H.R. Moutinho, T.A. Gessert, L.L. Kazmerski,* National Renewable Energy Laboratory

CdTe-based polycrystalline solar cells are leading candidates for terrestrial photovoltaic applications. High efficiency devices have been obtained despite large lattice mismatch between hexagonal CdS and cubic CdTe. Best CdTe based devices have been made with CdS/CdTe structure. Knowledge of the properties of the CdS/CdTe interface is critical to improve the understanding of the device as this interface lies close to the active junction in the device. In the present work, CdS was deposited by chemical bath deposition on Si substrates and CdTe was deposited by close spaced sublimation. Si substrates were used to facilitate the preparation of thin cross-sectional specimens for TEM analysis. The chemical nature of the CdS/CdTe interface, structural properties, and their dependence on the fabrication parameters e.g. substrate temperature (475-600°C) and post-deposition CdCl@sub 2@ heat treatment were analyzed. In addition, the effects of the interface structural defects on the crystallinity of CdS, prior to CdTe deposition, were examined. Small spot energy dispersive spectroscopy (EDS) of the interface revealed a considerable amount of sulfur in CdTe. The concentration of sulfur, in general, was higher in the grains with higher density of structural defects and at the grain boundaries. Planar defect density in CdTe films increased with substrate temperature while the threading dislocation density decreased. Interface analysis showed that the majority of the crystalline defects in the CdTe films, deposited on CdS, were generated at the interface. The crystallinity of CdS did not have major influence on the interface defect generation.

TF-MoP22 In-Plane Texturing in Evaporated Cr Films*, **J.F. Whitacre**,* University of Michigan*; Z.U. Rek,* Stanford Synchrotron Radiation Laboratory*; J.C. Bilello, S.M. Yalisove,* University of Michigan

The evolution of crystallographic texture in Cr films thermally evaporated using no energetic assistance was examined. In particular, the existence of an in-plane texture in films deposited onto obliquely oriented substrates was studied. All films were grown using electron-beam evaporation in a UHV chamber on (100) test-grade Si wafers with native oxide. The substrates were positioned such that their surface normals were oriented either 0° or 60° with respect to the adatom flux vector. Texturing, grain development, and surface morphology were studied using x-ray and electron diffraction, transmission electron microscopy (TEM), and scanning electron microscopy (SEM). The films grown on substrates oriented perpendicular to the flux vector developed a strong (110) out-of-plane texture, but showed no signs of in-plane texturing. These films had well-defined crystalline columnar grain structures and faceted surface morphologies. Those films grown on obliquely oriented substrates also displayed columnar grain structures and surface facets, though they were inclined ~35° with respect to the substrate surface normal. Despite this tilt, the out-of-plane texture was still (110). A heuristic model is proposed which describes the evolution of in-plane texture in evaporated films and accounts for the morphology and grain development observed. The combination of obliquely arriving adatoms and anisotropic surface facets creates an in-plane shadowing phenomena. If surface diffusion lengths are limited to grain dimensions, the model shows how grains with particular in-plane crystallographic orientations will grow at the expense of others. This process is modeled numerically and compared with experimental results. Work supported under ARO Army contracts DAAH 04-95-1-0120 and DAAG 55-98-1-0382. Some data collected at SSRL, funded by the US DoE.

TF-MoP23 Sputter Deposition of Ni Thin Films For Nickel Silicide Metallization*, **H. Zhang**,* Tosoh SMD, Inc.

NiSi is considered as one of the candidates to replace TiSi@sub 2@ contact in deep sub-miron metallization due to its low resistivity and lower formation temperature. Sputter deposition of Ni thin film is one of the crucial steps in nickel salicide (self-aligned silicide) process. One problem associated with sputter deposition of Ni is that Ni is a ferromagnetic material and is difficult to sputter. A Ni sputtering target results in low magnetic flux intensity in front of the target because the target shunts a considerable percentage of magnetic flux from system magnets. High magnetic flux density can be obtained by using a high pass-through flux (PTF) Ni target that allows maximum magnetic flux permeate through a target. In this study, the effects of target PTF and sputtering process parameters such as Ar pressure, sputtering power and substrate temperature on sputter process were studied. Ni targets with the PTF% of 40% (high PTF) and 30% (low PTF) were tested. Ni thin films were deposited on 200 mm (100) Si wafers. Sputter deposition rate, I-V characteristics, film sheet resistance and film uniformity were measured under various sputter conditions. The high PTF target resulted in low sputtering impedance and better Rs film uniformity. Rapid thermal processing (RTP) was carried out to form nickel silicides at temperatures between 300C to 900C for various times. Phases and microstructure of the films were characterized. The sheet resistance decreased significantly after annealing at 400C to 600C due to formation of NiSi. The significant increase in sheet resistance after annealing above 700C was attributed to formation of NiSi@sub 2@ phase.

TF-MoP24 Synthesis of Highly Oriented Piezoelectric AlN Films by Reactive Sputter Deposition*, **F. Engelmark**, G. Fuentes, I.V. Katardjiev, A. Harsta, U. Smith, S. Berg,* Uppsala University, Sweden

Nucleation and growth of polycrystalline AlN films on thermal and CVD oxide have been studied during RF reactive sputter deposition. The influence of the growth conditions, namely deposition pressure, RF power, Ar/N@sub 2@ ratio, substrate temperature, on film properties has been systematically studied. The properties of interest are crystallinity, degree of orientation, crystallite size, surface roughness, stress, piezoelectric coupling, acoustic velocity and others. The films have been analyzed with RBS, ESCA, XRD, ellipsometry, SEM, AFM, stress measurements, etc. It is found that these properties are sensitive functions of all deposition parameters and that there exist optimal deposition conditions under which films of high quality are obtained. The films at optimal conditions were analyzed with the following results: FWHM XRD 0.216 deg, FWHM rocking curve 1.62 deg, crystallite size 38 nm, optical index 2.15, surface roughness 31 Angstroms, stress 400 MPa. Further, to study the electro-acoustic properties of the films surface acoustic wave (SAW) filters were fabricated operating at 534 MHz. The thin film structure consists of AlN/SiO@sub 2@/Si. The electrodes of the interdigital transducers were made of Al. Examination of the frequency response indicated an acoustic velocity of 4900 m/s and a moderate coupling coefficient.

TF-MoP25 Surface Morphology Analysis in Correlation with Crystallinity of CeO@sub 2@(110) Layers on Si(100) Substrates*, **T. Inoue**, T. Nakamura, S. Nihei,* Iwaki Meisei University, Japan*; Y. Yamamoto,* Hosei University, Japan

In the course of the study on epitaxial growth of CeO@sub 2@ layers on Si(100) substrates, it is found that the layer has (110) orientation and requires substrate temperature above 820°C. Recently, we have succeeded in lowering growth temperature by more than 100°C by using newly developed "electron beam assisted evaporation". In general, epitaxial growth needs enough migration energy for adsorbed atoms and/or molecules. In the vicinity of the critical condition for epitaxial growth, CeO@sub 2@ layers having various crystallinity are obtained depending on growth conditions such as growth temperature, pre-treatment of the Si surface, contents of residual gas in the vacuum atmosphere and so on. It is very important to understand the growth mechanism, which rules crystallinity of the layer. We will present surface morphology analysis by atomic force microscopy (AFM) in correlation with crystallinity of the layers determined by reflection high energy electron diffraction (RHEED). It is clearly observed that surface morphology changes with crystallinity of the CeO@sub 2@ layers. Single crystal samples show a nanometer-scale-periodically corrugated sturcture, which consists of (111)-facets. On the other hand, the surface of poly-crystalline samples with a strong tendency of orientation consists of tetrahedral hillocks with irregular-rotational-orientations within the horizontal plane. Samples with a ring RHHED pattern show a very finely grained surface. These features clearly reflect the difference in the growth mechanism, especially at the early stage of the growth. Results on quantitative analysis of AFM data will be given.

TF-MoP26 Oxide Thin Films for Electroluminescent Phosphors*, **J.S. Lewis**, P.H. Holloway,* University of Florida

The use of oxide phosphors for thin-film electroluminescent (TFEL) displays has been investigated. Thin films of Zn@sub 2@GeO@sub 4@:Mn were deposited by RF magnetron sputtering from powder targets. The devices exhibited a brightness value of 85 cd/m@super 2@ versus 100 cd/m@super 2@ for the traditional ZnS:TbOF, another green emitting phosphor. The Zn@sub 2@GeO@sub 4@:Mn devices emit in the green with CIE color coordinates x = 0.30 and y = 0.66, which is a more saturated green than ZnS:TbOF. These data show that the performance of oxide phosphors rival that of the traditional sulfide based phosphors. Introduction of surface roughness and further optimization of processing should improve the values even further. Data from blue-emitting oxides will also be presented, as will injection layer schemes which should improve charge injection and lead to lower threshold voltages.

TF-MoP27 XPS and AES Investigation on the Oxidation Resistance of Plasma-treated Copper Leadframe*, A. Wong,* Nanyang Technological University, Singapore*; **R.G. Krishnan**,* Institute of Microelectronics, Singapore*; G. Sarkar,* Nanyang Technological University, Singapore

Copper is widely used as a material in the microelectronic plastic packaging and IC interconnect applications. The oxidation of copper to form oxide due to microelectronic processing can result in poor copper metal to epoxy mold compound (Cu/EMC) bonding causing package delamination which compromises package reliability. Besides, metallization material problems such as increment in signal transmission delays, decrease power dissipation and decrease reliability to electrical and thermal stress migration failures can occur. Plasma treatment of copper is believed to be able to enhance its oxidation resistance. Based on the x-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES) results, it was possible to confirm firstly, the successful incorporation of C and N into a copper film above the copper substrate using plasma treatment and secondly, the change in oxidation resistance of this film as a result of the treatment. Thickness measurements from AES depth profiles also confirmed the dominant influence the film thickness have on the enhancement of oxidation resistance in the film as compared to a small change in film stoichiometry. XPS and AES analyses show that once the film was heated at 250@super o@C, the N/Cu (atomic concentration) ratio of the film decreased from 1.074 to 0.635. Heating at 300@super o@C cause further decaying of the N/Cu ratio to to 0 which is confirmed by the disappearance of the XPS N 1s signal. There is no difference in the binding energy of the XPS Cu 2p3/2 signal of the pristine copper and the treated copper. The oxidation of pristine copper at 250 °C can be seen from the shift of the XPS Cu 2p3/2 binding energy at 932.70 eV to 933.60 eV and an increasing Full-width-half-maxima (FWHM) from 1.00 eV to 3.00 eV. However, these are not observed for the oxidation-resistant film at 250 °C as there is a delay in the oxidation onset temperature (shown by the shift in binding energy and increase in FWHM of the XPS Cu 2p3/2 spectra) by at least 50 °C, which depends on the film thickness. The surface analysis data and the oxidation resistance of the film are finally correlated and discussed.

TF-MoP29 Optimization of the Reflectivity of Magnetron Sputter Deposited Silver Films*, **M. Vergöhl**, N. Malkomes, B. Szyszka, F. Neumann, T. Matthée,* Fraunhofer Institute for Surface Engineering and Thin Films, Germany*; G. Bräuer,* Leybold Systems GmbH, Germany

Silver films were deposited by means of dc and mid-frequency (MF) magnetron sputter deposition on floatglass in order to achieve a maximum reflectivity over the entire visual and infrared spectral range. The films were investigated by means of ex-situ and in-situ spectroscopic ellipsometry, reflectivity, conductivity measurements, and atomic force microscopy (AFM). The following deposition parameters were varied: mid-frequency and dc-technique, power density, sputtering pressure, substrate temperature, sputtering gas (Ar, Kr, Ne), nitrogen and oxygen residual gas, and film thickness. With the aid of in-situ spectroscopic ellipsometry, it can be shown that for certain process parameters an optimum layer thickness exists for achieving a maximum reflectivity in the visual spectral range. With increasing thickness, optical losses come into play which are due to the formation of larger grains. This optimum layer thickness is smaller in the films deposited in the MF mode, indicating a smoother surface and smaller grain size compared to the DC mode. As an optimum value, a reflectivity of R=99.3% is achieved. The resistivity of this film was found to be @rho@=2.4 µ@Omega@ cm. The measured reflectivity is close to the theoretical value, which was determined from the Drude-Lorentz fit parameters with respect to the resistivity. The measured reflectivity of the sputter deposited films will be compared to thin films which are prepared by e-beam evaporation.

TF-MoP30 Preparation and Characterization of RF-sputtered SrTiO@sub 3@ Thin Films*, **K. Radhakrishnan**, C.L. Tan, H.Q. Zheng, G.I. Ng,* Nanyang Technological University, Singapore

Strontium titanate, SrTiO@sub 3@ (STO) material has found wide applications ranging from capacitor dielectrics in ICs to semiconductor memories and submicron ICs. This paper focuses on synthesis of STO thin films on Si and GaAs substrates under various growth conditions such as oxygen partial pressure and substrate temperature, and post annealing conditions. STO films were deposited by RF-magnetron sputtering in Ar/O@sub 2@ plasma. The substrate temperature was 200 to 300°C. Platinum was used as electrodes. The dielectric constant increased with increase in O@sub 2@ partial pressure during sputtering. However, it showed a decreasing trend when the partial pressure ratio, O@sub 2@/Ar was >1. The dielectric constant measured for these samples is low (14 to 22). X-ray diffraction measurements (XRD) showed peaks mainly due to substrate with weaker peaks corresponding to STO phase. The STO samples were annealed to study the effect of annealing on dielectric constant. The films were annealed for 1 hr under O@sub 2@ flow. It was observed that the dielectric constant was around 20 when the films were annealed below 500°C. However, when the temperature was above 500°C the dielectric constant value increased five times. A high value of 125 was measured for the film annealed at 600oC. The increase in the dielectric constant was due to the development of stable STO phase when annealed under O@sub 2@. Films annealed above 500°C showed intense XRD peaks corresponding to STO phase for (110), (200) and (211). The effect of film thickness on the dielectric constant was determined using 100 to 425nm thick samples. The dielectric constant increased from 117 to a high value of 145 when the thickness was 425nm. The average breakdown voltage measured capacitors with STO film thickness of 110nm was found to be 855kV/cm.

Applied Surface Science Division
Room 6A - Session AS-TuM
Ion Beam Analysis and Depth Profiling

Moderator: F.A. Stevie, Lucent Technologies

8:20am **AS-TuM1 Characterization of Shallow Junctions Using Secondary Ion Mass Spectrometry***, **C. Magee**, I.M. Abdelrehim, T.H. Buyuklimanli, J.T. Marino, W. Ou,* Evans East **INVITED**

As design rules drop below 0.25um, there is a need for developing methodologies to form ultra-shallow junctions for the source and drain extension areas of FETs. Ultra-low energy ion implantation and plasma doping appear to be the leading candidates to form these junctions. However, these techniques need to be followed by some kind of annealing step to activate the dopant. This talk will show how SIMS can be used to characterize the as-implanted distributions for ultra-low energy implants of B, P and As, as well to characterize the degree of dopant diffusion that occurs during annealing. This will be prefaced by a discussion of the problems inherent in SIMS analysis of such shallow structures. These problems arise from atomic mixing from the primary ion beam and surface roughening during the analyses.

9:00am **AS-TuM3 Quantitative Determination of Oxide Layer Thickness and Nitrogen Profiles for Si Gate Oxides***, **O. Brox**,* Universität Münster, Germany*; K. Iltgen,* AMD Saxony Manufacturing GmbH, Germany*; E. Niehuis,* ION-TOF GmbH, Germany*; A. Benninghoven,* Universität Münster, Germany

Accurate characterization of ultra-thin nitrided gate oxides is crucial for future semiconductor device scaling. We have investigated the capabilities of TOF-SIMS to control oxide thicknesses down to 2-3 nm and to quantify the nitrogen depth distribution. For all experiments we used the TOF III instrument, equipped with a flexible gas ion source and a cesium source (0.6 - 10 keV) for crater formation. An additional gas ion source (Ar@super@+, 11 keV) was applied for the analysis of the crater bottom. SiO@sub 2@ layer thicknesses can be determined by measuring exactly the position of the SiO@sub 2@/Si interface during depth profiling. This interface is indicated by drastic changes in the yield of the characteristic secondary ion species Si@sub x@O@sub y@@super -@. We found that the maximum in the Si- emission describes the position of the SiO@sub 2@/Si interface very exactly and that down to less than 3 nm oxide thickness a linear relationship exists between the position of this maximum and the oxide thickness as determined by TEM. We determined the nitrogen concentration in the oxide layers by following the nitrogen specific secondary ion SiN@super -@ and at the same time the SiO@sub n@@super -@ (n=0,1,2,3) intensities, which allow to calculate the corresponding lattice valency [1]. Relative sensitivity factors for nitrogen as a function of lattice valence were determined by using a nitrogen implant sample with a known nitrogen concentration. This allows to correct the measured SiN@super -@ profiles. We will report on these depth profiling results, the strong influence of the sputter ion energy on the width of the transient regime, changing between 1 nm for 0.4 keV and about 8 nm for 5 keV, on the influence of sample temperature during sputtering and on possible improvements by applying sputter ion energies @<=@ 0.4 keV combined with simultaneous Cs and noble gas sputtering. . @FootnoteText@ [1] C. Plog, L. Wiedmann, A. Benninghoven, Surf. Sci. 67 (1977) 565.

9:20am **AS-TuM4 Cesium Depth Profiling of Ultra-Shallow Implants***, **E. Niehuis**, T. Grehl, D. Lipinsky,* ION-TOF GmbH, Germany*; O. Brox, A. Benninghoven,* Universität Münster, Germany

Currently fabricated junction depths are between 50 nm and 100 nm, and they will decrease to about 10 nm for future deep sub-micron process technology. High depth resolution SIMS profiling is needed to control implant dose, junction depth, dopant distribution and its modification by thermal and chemical processes. In order to improve the depth resolution of SIMS, primary beam energies have been reduced over the last few years from several keV to a few hundred eV. In particular, oxygen depth profiling of B in Si in the sub-keV range has been studied in great detail over the last 2 years. In Cs depth profiling at low energies for the analysis of electronegative elements like As and P in Si two specific problems arise: 1. The decrease of the sputter yield with Cs energy results in a significant increase of the Cs surface concentration under steady state conditions. This has a strong influence on secondary ion emission and results in erosion rate changes in the transient regime. 2. A significant part of the implant dose is located in a native oxide or a screening oxide of the implantation process. Negative SI yields in a SiO@sub 2@ and Si matrix are quite different leading to errors in profile shape and implantation dose. We have investigated Cs sputtering at sub-keV energies using a TOF-SIMS instrument in the dual beam mode. A low energy Cs beam generates the sputter crater while a pulsed Ga beam at 15 keV energy probes the composition in the center of the crater. As the conditions of the analytical beam (energy, angle, spot size) are not changed with Cs beam energy, this dual beam mode is well suited for systematic studies in the very low energy regime. This paper will discuss the change of the positive and negative SI emission and erosion rate for SiO@sub 2@ and Si with Cs sputter energy. In addition, we investigate correction procedures in the transient regime and at the SiO@sub 2@/Si interface region.

9:40am **AS-TuM5 Characterization of Ultra-thin (2-3nm) Oxide Films using Low Energy Cs Ion Beams***, **D.F. Reich**, B.W. Schueler,* Physical Electronics*; J. Bennett,* Sematech, U.S.A

The thickness of silicon dioxide used as the transistor gate dielectric in most advanced memory and logic applications has decreased below 7nm, and is predicted to fall to 2-3nm for the next generation of devices. Characterization of thin oxide and nitrided oxide films by SIMS is currently achieved in quadrupole mass spectrometers using low energy primary Cs+ ions (0.75-2keV) at an angle of incidence of 60 degrees. Under these conditions, the preferred analysis method is to use MCs+ secondary ion monitoring in +SIMS, as this results in reduced matrix effects. For SIMS analysis of 2-3nm films, it is desirable to reduce the primary beam energy below 750eV, since the decay length and depth resolution even at this energy are comparable to the film thickness. Unlike the CsM+ results obtained with 0.75-2keV Cs+ beams at 60 degrees incidence, results with @<=@ 500eV Cs+ at angles from 60-75 degrees show matrix CsSi+ signals that are not in equilibrium in the near surface of the silicon substrate. By contrast, a 500eV Cs+ beam does result in constant matrix signals within the substrate when using ?SIMS. Interpretation of signals such as SiN- are, however, complicated by matrix effects at the oxide / silicon interface. The quadrupole SIMS instrument we are using employs ion columns with floating extractors. For the Cs column this results in useful primary beam currents of approximately 60nA at 500eV, and approximately 30nA at 250eV. Optimized off-axis extraction is possible using a split extractor when tilting the sample to vary the impact angle. To understand the CsM+ matrix signal variations at low primary energies, we report on measurements at Cs primary beam energies from 250-750eV, and at incidence angles of 60 and higher. Both +SIMS and -SIMS protocols are explored to understand optimum analytical conditions for characterization and quantification of 2-3nm ultra-thin oxides and oxynitrides.

10:00am **AS-TuM6 SIMS and XPS Correlation Study of Nitrided Gate Oxide***, **C.A, Bradbury**,* Micron Technology Inc., US*; C. Blackmer,* Micron Technology Inc.

Reliability of dielectric films such as silicon dioxide in the gate has become a key issue as MOS devices shrink in size. Many of the problems associated with reduction in both the width and thickness of the gate oxide can be controlled with the addition of nitrogen. Nitrogen incorporation into the oxide has been shown to have significantly better charge trapping properties, less interface state generation, and more resistance to continued oxidation and incorporation of impurities. The nitrogen also acts as a barrier to diffusion of dopants from the silicon substrate. The amount of nitrogen present and its location in the oxide control the extent to which each of these properties is exhibited. The concentration and distribution of nitrogen in gate oxides was studied using Secondary Ion Mass Spectroscopy (SIMS) and X-ray Photoelectron Spectroscopy (XPS). The SIMS analysis used Cs ion bombardment and detection of the CsN+ cluster to reduce the matrix effects associated with profiling from silicon oxide into silicon. A procedure was developed for XPS to provide the necessary signal to noise required for these low nitrogen concentrations. In addition to comparing the concentrations and spatial resolution of the nitrogen in the gate oxide, repeatability studies were also performed for each technique.

10:20am **AS-TuM7 Characterization of the Diffusion Properties of Metallic Elements Implanted into Silicon by SIMS***, **H. Francois-Saint-Cyr**, E. Anoshkina,* University of Central Florida*; F.A. Stevie,* Cirent Semiconductor/Lucent Technologies*; L. Chow, K. Richardson, D. Zhou,* University of Central Florida

Metallic elements introduced during device processing degradation or failure of semiconductor devices. Therefore, a better understanding of diffuison phenomena of metallic elements in silicon is useful for quality control and failure analysis. However, the diffusion data of many elements implanted into silicon are not readily available. Because of high sensitivity and excellent depth resolution, secondary ion mass spectrometry (SIMS) is the dominant analytical technique for determining the impurity profiles. When ion implantation, post-heat treatment, and SIMS analysis are combined, the diffusion characteristics of selected metallic elements can be better understood. A systematic investigation of the diffusion of Mg, Cl, K, Ge, Mo, Ca, Ti, V, Cr, and Mn has been carried out employing SIMS. These elements have been initially implanted into silicon wafers as low dose impurities, and then post-heat treatments of the ion-implanted samples have been conducted at different temperatures for a specific time. Following the post-annealing treatments, the depth-profiles of those elements have been obtained by the SIMS analyses. A wide range of diffusion behaviors has been observed for these elements. There possible, quantification of the diffusion process has been achieved based on the differences of the depth-profiles. Furthermore, the diffusion phenomena of different elements are discussed in terms of the activation energy, electronic structures and radii of ions, and their diffusion coefficients.

10:40am **AS-TuM8 Focused Ion Beam Micromachining of Thin Film Copper**, ***J. Phillips***, *D. Griffis, P.E. Russell,* North Carolina State University

The focused ion beam (FIB) sputtering behavior of thin film copper has been investigated as a function of tilt and rotation of the sample with respect to the incident ion beam. Thin film and single crystal copper was used for this study. The thin film samples were deposited by vapor deposition and shown by x-ray diffraction to be textured . A significant sputter rate increase was observed when milling textured copper at 12 degrees tilt, regardless of sample rotation. In an effort to understand the origin of this sputter rate enhancement, the orientation dependence of single crystal copper (111) was examined. Rotating the sample about [111] with various tilt increments (0-28 degrees in 4 degree steps) demonstrated that channeling effects were responsible for the increased sputter rate, as has been observed.@footnote 1@ In an effort to correlate the single crystal results with the thin film observations, (111) single crystal data was averaged over all rotations to give an overall material removal rate for each sample tilt. Data averaged in this manner directly correlates, within experimental error, with the thin film data suggesting that the crystallinity of the thin film copper is responsible for the observed sputter rate variation. Thus the FIB material removal rate of copper films can be increased by up to 30% by tilting the sample 12 degrees with respect to the ion beam axis. @FootnoteText@ @footnote 1@R. Behrisch, Sputtering by Particle Bombardment I, Springer-Verlag, New York, 1981, pp. 260, 300, 301.

11:00am **AS-TuM9 Surface Analysis and Depth Profiles of Self-healing Copper Aluminum Alloys***, ***J.F. Moore***, *W.S. Calaway, I.V. Veryovkin, M.J. Pellin,* Argonne National Laboratory

An investigation of the self-protecting properties of Cu@sub 3+x@Al@sub 1-x@ with ternary components (including small amounts of Ag, Ni, Mg, and Mn) is presented. When these alloys are heat treated, a self-terminated (micron-scale) layer rich in alumina is typically formed. The surface film, in principle, can protect the bulk alloy from chemical attack, for example in a molten salt, while maintaining desirable properties of conductivity and thermal stability. In this way the bulk and surface properties of the alloy may be separately optimized. Further, under these circumstances the film can regenerate if dissolved or damaged by rapid diffusion and oxidation of aluminum at the surface. To understand the properties of the initial thermal oxide, we have undertaken surface and depth profiling studies of these alloys using Auger and x-ray photoelectron spectroscopy and secondary neutral mass spectrometry. Results show a strong dependence of the surface composition with heat treatment temperature, alloy composition and oxygen environment. Depth profiling indicates a mixed, aluminum-rich oxide with long diffusion lengths for components in the bulk metal. @FootnoteText@ *Work supported by the U.S. Department of Energy, BES-Materials Sciences, under Contract W-31-109-ENG-38.

11:20am **AS-TuM10 Quasi Atomistic Depth Resolution with Auger Depth Profiling for Oxide / Metal Structure**, ***M. Menyhard***, *A. Barna, Zs. Benedek, A. Sulyok,* Research Institute for Technical Physics and Materials Science, Hungary

By applying specimen rotation, and grazing angle of incidence for depth profiling, the depth resolution is limited by atomic mixing. To achieve depth resolution of less than 1 nm we have two possibilities; either to decrease the ion energy or to find evaluation routine to correct the effect of atomic mixing. Using very low ion energy, however, the sputtering rate is small resulting in practical problems e.g. extreme cleanliness long measuring time is necessary. Thus it is of great importance to develope evaluation routines for the correction of atomic mixing. We have shown that our trial-and-error routine based on dynamic TRIM simulation can be successfully applied@footnote 1,2@ for the evaluation of the depth profiles where the layers are made of elements with no affinity for compound formation. In this contribution we will report on the extension of our evaluation method for the case of oxide / metal structure. Well characterized silicon oxide /silicon, and oxynitride / silicon structures (specimens were kindly provided by E. Garfunkel of U. Rutgers) with various thickness were depth profiled applying various sputtering conditions. At 0.4 keV Ar sputtering (where the measurement time is reasonable) the depth resolution was found to be around 0.7 nm, while at 0.2 keV better than 0.4 nm. At this later energy, however, practical studies cannot be performed because of the long measuring time. Our evaluation routine was parametrized to reproduce the experimentally measured depth profiles for a given sputtering condition. It turned out that using the same parameters the simulated and measured depth profiles agreed well for the various sputtering conditions. In this way we can apply the higher ion energy (0.4 keV) for routine analysis and using the evaluation routine depth resolution about 0.4 nm could be obtained. @FootnoteText@ @footnote 1@M. Menyhard, Surf. Interface Anal. 26 1001 (1998). @footnote 2@M. Menyhard and A. Sulyok, J. Vac. Sci.Tech A16 1091 (1998).

Biomaterial Interfaces Group
Room 613/614 - Session BI-TuM

Protein Solid-Surface Interactions II

Moderator: J.L. Brash, McMaster University

8:20am **BI-TuM1 Functionality of a Model Protein at Nanostructured Surfaces**, ***D.S. Sutherland,*** Chalmers and Gothenburg University, Sweden; *M. Broberg, H. Nygren,* Gothenburg University, Sweden; *B. Kasemo,* Chalmers and Gothenburg University, Sweden

Nanofabricated surfaces can be used to study the influence of surface topographic features on the behaviour of a model protein. Colloidal lithography was used with simple lift-off steps to create surfaces with defined nanotopography. The functionality of equal-quantities of fibrinogen molecules bound at surfaces containing pits of 40nm diameter or 110nm diameter was probed. The kinetics of binding of unactivated platelets to these surfaces from a static albumin-containing buffer was used as a measure of the functionality/conformation of the fibrinogen molecules. Two sets of samples were prepared, one where the surfaces were chemically homogeneous (titanium oxide) and one where the surfaces additionally contained nanodomains of gold coated in a methyl-terminated self-assembled monolayer at the base of the pits. Platelet binding on fibrinogen adsorbed at flat surfaces and surfaces with 110nm diameter pits showed relatively low binding rates which were not significantly different than that found at control surfaces (with no adsorbed fibrinogen). By contrast platelet binding on fibrinogen adsorbed at surfaces containing 40nm diameter pits gave significantly higher binding rates than both other test surfaces and control surfaces. For these samples with 40nm diameter pits similar results were obtained for both surfaces with homogeneous chemistry and for chemically nanodomained surfaces. These results are interpreted to mean that fibrinogen molecules bound at surfaces with 40nm diameter pits have altered conformation or orientation (compared to flat surfaces or surfaces with larger pits) to make available platelet-binding sites. These pits are smaller that the reported characteristic size of fibrinogen molecules (46-55nm length) and it appears that the effect is the result of topography rather than surface chemistry. These model experiments indicate that the conformation/orientation of individual protein molecules can be influenced by like-sized surface features.

8:40am **BI-TuM2 Hierarchical Ordering of Proteins at Interfaces with a Nanoscale Surface Topography**, ***V. Vogel***, *L. Smith, T. Nguyen, J.R. Dennis,* University of Washington

Elucidating mechanisms by which to control the ordering of proteins at interfaces is of fundamental importance in bioengineering and biotechnology. Whereas major progress has been made recently in stabilizing proteins at interfaces in their native states, and in controlling their orientation, much less is known how to promote their spontaneous self-assembly into a structurally well controlled supramolecular architecture. Here we discuss that nanoscale topographic surface features with ridges the size of natural ECM fibrils have a pronounced impact on protein adsorption, and on the spatial alignment of human dermal fibroblasts and cell-deposited collagen fibrils. Furthermore, by elevating cells above the surface such that they deposit collagen through a porous membrane onto the nanoscale ridges without being in physical contact with the surface, the role of the cells has been separated from the role of topography in collagen type VI deposition and fibrillogenesis. Insight into the mechanisms by which synthetic surfaces manipulate the hierarchical organization of ECM fibrils will be crucial in the rational design of the surface topography of biomaterials and of scaffolds for tissue engineering.

9:00am **BI-TuM3 Protein Adsorption on Solid Surfaces : From Static to Dynamic Properties***, **P. Schaaf**,* Institut Charles Sadron, France **INVITED**

Adsorption processes of proteins on solid surfaces have been investigated over many years but, due to their complexity, it is still difficult to predict their behavior. Indeed, proteins are highly structured polyelectrolytes, polyamphiphiles, which, in addition, are often only marginally stable. While interacting with a solid surface, they often change their structure and parallelly increase their anchoring to the surface. The influence of different parameters entering in these adsorption processes, such as the substrate charge, the substrate hydrophobicity and the protein stability, will be discussed. The dynamics of these processes will, in particular, be mentionned. It will appear that the time scales entering in adsorption processes range from tens of hours down to milliseconds. While the characteristic interaction time needed for fibrinogen, a plasma protein, to bind to a silica surface appears to be of the order of 50ms, the exchange ability of a ribonuclease molecule adsorbed on a titanium oxyde surface changes with a characteristic time of the order of 10 hours. Structural changes are observed in the adsorbed layer over similar time scales. Recent results obtained in this field, in particular by Infrared Spectroscopy and by Atomic Force Microscopy, will be presented

9:40am **BI-TuM5 Protein Adsorption Kinetics: Particle Model and Optical Experiment***, M.A. Brusatori, C. Calonder, **P.R. Van Tassel**,* Wayne State University

The adsorption of proteins at the liquid-solid interface is a phenomenon of great importance in bioseparations, biocatalysis, and materials biocompatibility. Adsorption is often accompanied by a surface-induced transition in either internal conformation or molecular orientation. Recently, Van Tassel, et al, presented a model in which the adsorption/ transition process is modeled as the sequential surface placement of spreading disks. In this talk, we present a derivation of analytical expressions for the adsorption and spreading probabilities, whose use greatly simplyfies the form of the kinetic equations for this model, using the scaled particle theory (SPT). We also present new experimental data of fibrinogen adsorption onto SiTiO2 and dextran-coated SiTiO2 using optical waveguide lightmode spectroscopy (OWLS). We show that the SPT spreading disk model can accurately predict these and other experimental data as well as those from computer simulation.

10:00am **BI-TuM6 Probing Immobilized Protein Peptide Architectures***, **S.J.B. Tendler**, M.M. Stevens, W.C. Chan, M.C. Davies, C.J. Roberts, P.M. Williams, S. Allen,* University of Nottingham, U.K.

The ability to control the assembly of molecular architecture at the nanometre scale is an important research goal. Complex molecular assemblies can be designed and constructed to have applications in several bio-analytical fields, for example, as key components in devices such as biosensors and affinity-based chromatographic supports. We have demonstrated the creation of a higher order molecular assembly which consists of a bis-biotinylated peptidic spacer between two streptavidin molecules. This molecular architecture exploits the strong affinity between streptavidin and biotin to promote self-assembly. Surface plasmon resonance has enabled us to monitor the construction of the multilayer in real time. Atomic force microscopy has been utilized to measure adhesion forces between biotinylated bovine serum albumin functionalized probes and the surface at each stage of the multilayer assembly. This facilitated the determination of surface functionality and associated mechanical properties at each of these stages. An increase in the elasticity of the system was observed once the multilayer was created. It is postulated that unraveling of an alpha-helical component in the conformation of the peptide before rupture of the streptavidin-biotin link may contribute to the increase in molecular elasticity of the multilayer. We have also demonstrated through a trifluoroethanol titration monitored by circular dichroism that variations in the solvent can affect the secondary structure of the peptide linker and hence its mechanical properties. These observations have wide implications for protein immobilization in terms of the precise control of distances of active layers, steric surface barriers, underlying surface forces and hence biological functionality.

10:20am **BI-TuM7 New Platform Technology for the Investigation of Initial Interaction of Adsorption and Cross Linking of Strong Adhesives at Solid Surfaces***, **H. Elwing**, F. Hook,* Goteborg University, Sweden

The contacting area between an implanted biomaterial and the surrounding tissue is of critical importance for the functional success of the biomaterial. We try to develop tissue "glues" and we get our biomimic inspiration from marine organisms. Several marine animals and plants living at hard rocks, or man made material have developed successful glues or adhesives for contacting the hard surface. There must be at least two conditions fulfilled for strong adhesion of marine organisms to a flat solid surface. Firstly there must be sufficient strength of molecular adhesion at the liquid/solid interface. Secondly it is required that the adhered molecules are cross-linked at the surface and into the tissue of the organism. We have concentrated our effort to understand more about the cross-linking mechanisms. Unfortunately there are few methods available for measuring cross-linking of biopolymers in real time, which have made research difficult. Consequently, as a first step we have developed a methodological combination of surface plasmon resonance (SPR) and Quarts chrystal microbalance (QCM-D) for simplified analysis of adsorption and cross-linking of marine adhesives, such as mussel adhesive proteins and Barnacle cement, adsorbed as monolayers on flat solid surfaces.

10:40am **BI-TuM8 Molecular Orientation Distributions in Submonolayer Films Corresponding to Quasi-Reversible Electron Transfer Behavior***, S.S. Saavedra, **R.T. Robertson**, N.R. Armstrong, S. Mendes,* University of Arizona

The relationship between the molecular orientation distribution and the electron transfer behavior of immobilized redox proteins has been investigated through the use of novel waveguide-based spectroelectrochemical methods. The ability to probe the electron transfer behavior which corresponds to a particular molecular orientation will provide significant insight into the fundamental electron transfer processes that occur in physiological systems. The orientation geometry is obtained using an electroactive integrated optical waveguide (EA-IOW) format coupled with electroactive total internal reflection fluorescence (EA-TIRF). Orientation distributions of horse heart cytochrome c corresponding to quasi-reversible electron transfer have been characterized and will be discussed here.

11:00am **BI-TuM9 Surface Orientation of Peptides with @alpha@-helix and @beta@-sheet Secondary Structures on Fluorocarbon Substrates***, **L. Gamble**, J.R. Long, P.S. Stayton,* University of Washington*; D.A. Fischer,* National Institute of Standards and Technology*; D.G. Castner,* University of Washington

The orientation of surface bound proteins can have a significant effect of their function. To aid with the interpretation of Near edge X-ray absorption fine structure (NEXAFS) spectra from adsorbed protein films we haved studied short, well-defined peptide "standards." NEXAFS is a surface sensitive technique that has been used to determine the orientation of polymers and self-assembled monolayers. Here NEXAFS is used to determine the surface orientation of short peptides chains designed to adsorb in @alpha@-helical and @beta@-sheet conformations on hydrophobic surfaces. The N K-edge spectra show an orientation dependence of the N1s to @pi@* peak between the 90° and 20° incident x-ray angles for both peptides adsorbed onto highly-ordered poly(tetrafluoroethylene) (PTFE) surfaces. The results indicate that the @beta@-sheet peptide is adsorbed with the peptide backbone "parallel" to the substrate, while the @alpha@-helix adsorbes with the helical axis parallel to the substrate. Spectra of the O K-edge support these results. The lack of orientational dependence seen for these same peptides adsorbed onto a disordered fluoropolymer surface containing different types of fluorocarbon species indicates the degree of substrate order and/or the type of surface functional groups play a key role in determining the degree of ordering in the adsorbed peptides. NEXAFS spectra were also used to distinguish between the secondary structures of the two peptides. Preliminary NEXAFS results from adsorbed protein films show that orientataion of the peptide backbone is only observed for non-gobular proteins such as fibrogen and fibronectin. Gobular proteins such as albumin do not exhibit any preferrential orientation, even on highly-ordered substrates.

11:20am **BI-TuM10 A Multi-Parameter QCM Technique for Investigations of Protein and Surface Interactions***, **F. Höök**,* Chalmers Univ. of Tech. and Göteborg Univ., Sweden.*; M. Rodahl,* Q-Sense AB, Sweden*; B. Kasemo,* Chalmers University of Technology, Sweden

Protein molecules in contact with solid, non-biological materials, is a situation of broad scientific interest and technological importance, and there is a growing need for new tools to study these interactions. For instance, if the influence from the surface is large enough, the conformational-free-energy minimum for a protein attached on a surface might correspond to a conformation that differs from that of the native protein. It is thus likely that a protein-surface interaction might affect the conformation and hence the function of the proteins. We have developed a sensor system based on the traditional quartz crystal micro balance (QCM) technique, but where both the resonant frequency (f) and the energy dissipation (D) are measured simultaneously for a non-driven (freely oscillating) sensor crystal. This offers a possibility to investigate changes in the viscoelastic properties of adsorbed proteins in real time, which are further directly related to the conformation of the adsorbed proteins. Examples of how this type of measurements contributes with such information are presented using examples of: (i) Hemoglobin (Hb) adsorbed with and without the ligand carbon monoxide, which is known to slightly effect the conformation and stability against denaturation of Hb in solution. (ii) Antibody-antigen reactions, where we emphasize the added value from this type of multi-parameter analysis for immuno-sensing or of recognition events in general. (iii) Adsorption and enzymatic induced cross-linking of a mussel adhesive protein. We also demonstrate how additional information about these and similar types of measurements are obtained by simultaneously also measure at different frequencies, since different conformational states in some situations respond differently at different frequencies. We also demonstrate the importance of multi-parameter analysis in order to be able theoretically treat the QCM response upon adsorption of non-rigid biomolecules.

11:40am **BI-TuM11 Probing the Oxidation of Amine Modified Surfaces by MALDI Mass Spectrometry*, G.R. Kinsel*,** *R.B. Timmons, A.K. Walker, Y. Wu,* University of Texas, Arlington

The oxidation of amine modified surfaces, produced by pulsed RF plasma polymerization of allyl amine, can lead to substantial changes in the interaction of these surfaces with peptides and proteins in solution. Initial studies, using matrix assisted laser desorption / ionization (MALDI) mass spectrometry to characterize surface-peptide retention affinity, suggest that theses changes result from the acquisition of significant acidic character by the surface during the oxidation process. We have undertaken a variety of studies designed to characterize the surface chemical changes resulting from exposure of amine modified surfaces to air and to quantitate the impact of these changes on the peptide retention affinity. In these studies amine modified surfaces were exposed to pure oxygen and pure carbon dioxide environments. Time dependent changes in surface chemistry were monitored by FTIR spectroscopy and global compositional changes in surface chemistry were monitored by X-ray photoelectron spectroscopy. Subsequently, surface-peptide retention affinities were determined as a function of solution ionic strength and surface oxidation by using MALDI mass spectrometry. In addition, MALDI mass spectrometry was used to directly characterize oxidative changes in low duty cycle allyl amine polymer films to gain insight into the nature of the chemical modifications occurring in these polymer films. The results of these studies provide unique insight into the specific chemical changes and stability / reactivity of these surface modified materials.

Electronic Materials and Processing Division
Room 608 - Session EM-TuM

Si Surface Chemistry and Etching, Passivation, and Oxidation

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

8:20am **EM-TuM1 Structural Transition Layers at the Interface of SiO@sub 2@/Si(100) Fabricated by Ozone*, K. Nakamura*,** *H. Itoh, A. Kurokawa, S. Ichimura,* Electrotechnical Laboratory, Japan*; K. Koike, G. Inoue, T. Fukuda,* Iwatani International Corporation, Japan

A novel processing technique for oxidation with rapid growth kinetics at lower substrate temperature is strongly required to fabricate a much thinner silicon dioxide film 1nm thickness. This was confirmed by a change of the etching rate of SiO@sub 2@ film with dilute hydrofluoric acid solution. Such thinner region of transition layers in the ozone-oxide was implemented either on clean Si(100)2x1 or on Si(100) with an already existing native oxide film at 300°C or more. However, exposure of ozone to Si(100) with an already existing thermally grown oxide film, for example at 350°C, caused no change in the distribution of transition layers in the oxide. This contrast indicates that the oxide growth by ozone or the further oxidation of lower oxidized silicon atoms in the native oxide by ozone formed transition layers with much less thickness, while highly oxidized silicon atoms in the thermally grown oxide film remained unreacted even by reactive ozone. Structural transition layers on the opposite side of the interface, i.e. in the substrate, will also be discussed.

8:40am **EM-TuM2 Infrared Spectroscopy as a Probe of Semiconductor/Dielectric Interfaces: Growth and Structure of SiO@sub 2@ on Si*, K.T. Queeney*,** *M.K. Weldon, Y.J. Chabal, K. Raghavachari,* Bell Laboratories, Lucent Technologies **INVITED**

The structure and quality of the Si/SiO@sub 2@ interface are crucial to the performance of transistors with gate oxide thicknesses < 20 Å. We have exploited the intrinsic sensitivity of infrared absorption spectroscopy to microscopic chemical environment in order to elucidate structural details of this interface between crystalline Si and amorphous SiO@sub 2@. Infrared spectra of thermally grown SiO@sub 2@ are acquired as a function of film thickness by etchback of device-quality films. Modeling the mechanical and optical properties of these films reveals that substoichiometry at the Si/SiO@sub 2@ interface dominates the spectra of ultrathin (< 10 Å) SiO@sub 2@; different thermal histories are shown to affect the quality of this "transition region." To understand the microscopic structure of this interfacial substoichiometry, we have grown and characterized a model Si/SiO@sub x@ interface via controlled H@sub 2@O reaction of Si(100)-(2x1) in ultrahigh vacuum. Coalescence of dimer-based silicon epoxide species (capped by triangular Si-O-Si linkages) into an extended silicon-oxygen network results in the birth of SiO@sub x@ phonon modes (975 and 1130 cm@super -1@) whose microscopic structural origins are for the first time well understood. This epoxided interface is trnasformed at room temperature into high-quality SiO@sub 2@, and the mechanism for room-temperature H@sub 2@O-induced oxidation is compared to that observed for technologically relevant surface terminations.

9:20am **EM-TuM4 Real Time Observation on Si(001) Surface Oxidation by Scanning Tunneling Microscopy*, K. Miki*,** Electrotechnical Laboratory, Japan*; Y. Kudo, M. Murata, K. Yamabe,* Tsukuba University, Japan

We have succeeded in real time observation on oxidation of Si(001) surface by scanning tunneling microscopy at elevated temperatures up to 1100 K. First we made clear the boundary between etching and oxidation regions. At the 900 K, etching both from step edges and in the terrace was dominant at low oxygen partial pressure under $1 \times 10^(-5) Pa$ while we observed oxidation island nucleation over this critical pressure. Under low rate oxidation, we found that etching is allowed together and it stops in the vicinity of the oxidation island. Our map whether etching or oxidation occurs is consistent of the previous reports. At the high temperature region the boundary is good agreement with the previous report by Gelain and et al. [Oxidation of metals 3 (1971) 139]. In the low temperature region under 870 K the oxidation speed of the first 1 ML is independent of temperature and this results is consistent with reflection electron microscopy experiment by Watanabe and et al. [Phys. Rev. Lett. 80 (1998) 345] We found three types of absorbant. Although the one type is still a misery, we could identify that one is atomic oxygen adsorbant in the center of a Si dimer and the other is back bond oxidation. First one was well seen in the initial stage, as oxidation proceeded the latter became more dominant. This observation suggests that oxidation of Si(001) surface has dual species at least, which is previously reported by Engstrom and et al. [Surf. Sci. 256 (1991) 317]. Backbond oxidation extended normal to dimer rows as ordered spots. The ordering eventually came to have disordering around 1ML oxidation. This suggests that stress during is very important even in the initial stage.

9:40am **EM-TuM5 Scanning Tunneling Microscopy Study of Surface Morphology of Si(111) after Synchrotron Radiation Stimulated Desorption of SiO@sub 2@*, Y. Gao*,** *T. Miyamae, H. Mekaru, T. Urisu,* Institute for Molecular Science, Japan

We have used scanning tunneling microscopy to investigate the surface morphology of Si(111) after the native SiO@sub 2@ layer was removed by synchrotron radiation stimulated desorption at 650 °C. The surface shows large regions of atomically flat Si(111)-7x7 structure. An interesting feature of the surface is the formation of atomic steps nicely registered to the crystal structure, and the pinning of the steps by nanometer scale dust is evident. This is in sharp contrast to Si(111) surfaces after thermal desorption of SiO@sub 2@ at temperatures 880°C and above, where the surface steps are much more irregular. The registration of the surface steps to the underlying crystal structure indicates that the surface atomic layer reaches thermodynamic equilibrium under synchrotron radiation at temperatures much lower than that necessary for thermal desorption of SiO@sub 2@.

10:00am **EM-TuM6 How Important are Second Nearest Neighbor Effects in Silicon 2p Photoemission Spectroscopy of Si/SiO@sub 2@ Interfaces?***, **J. Eng, Jr.**, K. Raghavachari,* Bell Labs, Lucent Technologies

The proper interpretation of Si 2p photoemission spectra of Si/SiO@sub 2@ interfaces has been a controversial topic since 1993, when Banaszak-Holl and McFeely proposed that second nearest neighbor effects can cause significant chemical shifts in Si 2p photoemission features.@footnote 1@ Their claims were based upon model Si/SiO@sub 2@ surfaces produced by the adsorption of H@sub 8@Si@sub 8@O@sub 12@ clusters on Si(100) at room temperature. Arguing that the clusters are bonded to Si(100) dimers through a single vertex (due to Si-H bond cleavage), they proceeded to correlate the relative peak positions and peak intensities with different Si species at the interface. This correlation led them to conclude that the entire formal oxidation state framework is inadequate for interpreting Si 2p photoemission spectra of Si/SiO@sub 2@ interfaces, and that second nearest neighbor effects are important. The key issue in this controversy is understanding how the H@sub 8@Si@sub 8@O@sub 12@ clusters bond to the Si(100) surface. Using transition state calculations, we present detailed mechanistic arguments which show that the clusters do not react with the Si(100) surface through Si-H bond cleavage, but rather through Si-O bond cleavage. The resulting "cracked" cluster allows us to predict the Si 2p photoemission features of the clusters on Si(100) using the conventional formal oxidation state model, without invoking second nearest neighbor effects. Finally, the normal mode frequencies of the "cracked" cluster are in excellent agreement with infrared studies of the clusters on Si(100). @FootnoteText@ @footnote 1@ M. M. Banaszak-Holl and F. R. McFeely, Phys. Rev. Lett., 71(15) (1993) p.2441.

10:20am **EM-TuM7 FTIR Studies of the Nitridation of Si(100)-(2x1) and Oxidized Silicon***, K.T. Queeney, **Y.J. Chabal**, J. Eng, Jr., K. Raghavachari,* Bell Laboratories, Lucent Technologies*; X. Zhang, E. Garfunkel,* Rutgers University*; S.B. Christman, E.E. Chaban,* Bell Laboratories, Lucent Technologies

We have investigated the incorporation of N into Si and SiO@sub 2@ with IR absorption spectroscopy, in order to elucidate the mechanisms by which nitridation and oxynitridation influence the structure and thus the electrical characteristics of Si/SiO@sub 2@ interfaces. Studies of the adsorption and decomposition of NH@sub 3@ on Si(100)-(2x1) demonstrate that the chemistry of this nitriding agent is governed by a combination of dissociative and molecular adsorption, with metastable NH@sub 3(a)@ characterized by a dramatically redshifted NH@sub 3@ deformation mode. Higher coverages and temperatures favor NH@sub 3@ dissociation into H and NH@sub 2@, followed by competing desorption and decomposition. The mechanism for N insertion into the Si substrate is studied via repeated cycles of NH@sub 3@ dosing and annealing with post-dosing of atomic H to identify discrete N-containing structures by the perturbation in @nu@(Si-H) frequencies. Oxynitride growth by reaction of NO on Si(100)-(2x1) reveals the interplay between oxygen and nitrogen, as both Si-O (~900 cm@super -1@) and Si-N (~775 cm@super -1@) modes exhibit frequencies distinct from those observed for pure oxide and nitride films. These fundamental growth studies are used to interpret structural details contained in the complex spectra of device-quality nitride and oxynitride films grown on Si.

10:40am **EM-TuM8 Silicon Passivation Chemistry for MEMS Technology***, **R. Maboudian**,* University of California, Berkeley **INVITED**

Adhesion, friction , and wear are prevalent problems in a majority of micro-electro-mechanical systems (MEMS) devices. Since gravity is negligible at the dimension of most microstructures, understanding of surface interactions in MEMS is of paramount importance for controlling stiction phenomena. After a brief introduction to Si micromachining, I will discuss the use of various micromachined testing devices, such as cantilever beam arrays, in conjunction with other surface characterization techniques, such as X-ray photoelectron spectroscopy and atomic force microscopy, to measure the surface forces present between polycrystalline silicon surfaces and to manipulate them by utilizing various surface passivation treatments.

11:20am **EM-TuM10 STM Studies of the Site-specific Reactivity of Isopropanol in Aqueous Silicon Etching: Controlling Morphology with Surface Chemistry***, **M.A. Hines**, T.A. Newton, Y.-C. Huang, L.A. Lepak,* Cornell University

Aqueous silicon etchants play an important role in the fabrication of microelectromechanical systems (MEMS). To improve performance, a reputedly inactive chemical agent -- isopropanol [(CH@sub 3@)@sub 2@CHOH] -- is often added to the etchant. Not only does this simple additive reduce undercutting by up to 75%, it also produces much smoother etched surfaces, in part by suppressing the formation of pyramidal etch hillocks. Using a combination of STM measurements and kinetic Monte Carlo simulations, we will show that these morphological changes have a simple, chemical origin. The site-specific rates of isopropanol reaction on vicinal Si(111) surfaces were studied by kinetic competition with an etchant of known anisotropy and quantified using concentration-dependent changes in the etched surface morphology. The unique properties of isopropanol-enhanced etchants are explained by the relatively high reactivity of the isopropoxide ion. Once formed, the silicon isopropoxy species transiently suppresses etching at specific surface sites and modifies the anisotropy of the etchant.

11:40am **EM-TuM11 Removal of Native Oxide Employing Heated NH@sub 3@/NF@sub 3@ Mixture***, **H. Ogawa**,* The University of Tokyo, Japan*; T. Arai, T. Ichiki,* Toyo University, Japan*; Y. Takamura, Y. Horiike,* The University of Tokyo, Japan

The removal of the native oxide employing a heated NH@sub 3@/NF@sub 3@ mixture was studied using in-situ XPS and FTIR-ATR/RAS. The mixture was heated in an 13 mm diameter Al@sub 2@O@sub 3@ tube whose surface was wound by a resistive heater, then being exposed to a sample set on a stage cooled by a N@sub 2@ gas with room temperature. The chemical oxide was grown in a H@sub 2@SO@sub 4@/H@sub 2@O@sub 2@ solution. The NH@sub 3@/NF@sub 3@ mixture with partial pressure ratio of unity at a pressure of 1 Torr started to remove the oxide from a Al@sub 2@O@sub 3@ tube temperature of 500 °C. For the Si surface after removal of the oxide, new XPS peaks appeared at 103.8 eV in Si2p and 402.2 eV in N1s, respectively. Absorption spectra of Si-H(2100 cm@super -1@), N-H(stretching; 3330 cm@super -1@, bending;1454cmcm@super -1@) and Si-F (783 cm@super -1@) were also observed in the IR measurement. These results exhibit the presence of a (NH@sub 4@)@sub 2@SiF@sub 6@ film deposited on the Si surface after removal of the oxide.@footnote 1@The film desorbed readily at 100 °C in a vacuum and then was terminated by hydrogen. The higher the partial pressure, the faster the oxide removal rate, whereas NH@sub 3@ or NF@sub 3@ alone did not demonstrate any etching reaction. The result that the Al@sub 2@O@sub 3@ tube heated at higher temperature led to the higher etch rate implies generation of the oxide etchant within the tube. Thus, NH@sub 3@ and NF@sub 3@ were introduced separately to two tubes, and when NF@sub 3@ alone was heated, the present reaction was confirmed. The result implies thermally decomposed NF@sub 3@ reacts with NH@sub 3@, generating the oxide etchant. The removal rate ratio of thermal grown SiO@sub 2@ to BPSG (boron phosphorus silicate glass) films was almost unity. It is well known that the usual HF solution produces about ten times higher etch rate for BPSG than for the thermal SiO@sub 2@. Accordingly, this technology allows us to offer a new dry cleaning method of the contact hole surface in ULSI multi-level interconnection process. @FootnoteText@ @footnote 1@M. Hirose, S. Yokoyama and Y. Yamakage: J. Vac. Sci. Technol., B3 (1985)1445.

Flat Panel Displays Topical Conference
Room 604 - Session FP-TuM

Novel Materials for Field Emission Displays and Technologies for Flexible Displays

Moderator: B. Gnade, DARPA

8:20am **FP-TuM1 Comparative Study of Field Emission from Microcrystalline Graphite, Nanostructured Graphitic Films, and Nanotubes***, **A.A. Talin**, K.A. Dean, B.F. Coll, J.E. Jaskie, M. Johnson,* Motorola Flat Panel Display Division

Electron emission at remarkably low electric fields has been reported from a wide variety of carbon films over the past decade. Although the precise mechanism of emission is still under debate, it is becoming clear that graphitic phases of carbon play a central role in the origin of the low-field emission properties of carbon-based cold cathodes. In this work, we use conventional diode type apparatus to measure broad-area emission characteristics, and field emission microscopy to investigate and identify the carbon phases associated with field emission. We demonstrate that purely SP2 carbon films can be excellent field emitters. We relate the differences in broad area field emission characteristics and in field emission microscopy images in terms of film morphology and the field emission physics of various carbon phases. .

8:40am **FP-TuM2 Demonstration of Low Work Function Cu-Li Alloy Coatings for Edge Field Emission Devices@footnote *@**, ***J.C. Tucek***, *A.R. Krauss, O. Auciello, D.M. Gruen, D.C. Mancini, N. Moldovan,* Argonne National Laboratory

Low work function alkali metals have been shown to significantly enhance field electron emission when used as coatings for microtip field emission arrays (FEAs). Maximum enhancement of electron emission is expected for alkali metal coatings 0.5-1 monolayer in thickness. 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. We have recently demonstrated that lithium alloy coatings based on materials developed at Argonne National Laboratory provide very stable, low work function coatings with low threshold field (~ 3 V/µm) and enhanced electron emission for application to FEAs.@footnote 1@ These alloy coatings maintain a segregated monolayer of lithium on the surface of the alloy, even under adverse environmental conditions or ion bombardment. As an extension of this work, Cu-Li coated edge emitters are produced by coating Si posts, followed by ion beam sputtering of the alloy and a selective etching of Si, resulting in the formation of hollow cylinders with nanometer thick Cu-Li walls. It can be expected that Cu-Li edge emitters will provide a larger emitter area, and therefore should be more robust than the Si FEAs while maintaining a similar low field emission threshold. In addition, we have performed tests using a simulated flat panel display configuration, which provide information about the emission uniformity of these edge emitters. The emission characteristics of the new Cu-Li-based edge emitters will be discussed in relation to the alloy composition and the geometry of the emitters. Re abstract entitled "Demonstration of Low Work Function Cu-Li Alloy Coatings for Edge Field Emission Devices" by J.C. Tucek et. al., submitted for presentation at the 46th International Symposium of the American Vacuum Society, Seattle, Washington, October 25-29, 1999, please be advised that: The submitted manuscript has been created by the University of Chicago as Operator of Argonne National Laboratory ("Argonne") under Contract No. W-31-109-ENG-38 with the U.S. Department of Energy. The U.S. Government retains for itself, and others acting on its behalf, a paid-up, nonexclusive, irrevocable worldwide license in said article to reproduce, prepare derivative works, distribute copies to the public, and perform publicly and display publicly, by or on behalf of the Government. @FootnoteText@ @footnote 1@ O. Auciello, et. al., J. Appl. Phys. (in press, 1999). @footnote *@ Work supported by the U.S. Department of Energy, BES-Material Sciences, under Contract W-31-109-ENG-38 and DARPA/ONR under contract N00014-97-F0905.

9:00am **FP-TuM3 Progress and Performance of FEAs using Zirconium Carbide Field Emitters**, ***W.A. Mackie***, *T. Xie, P.R. Davis,* Linfield Research Institute

Field emission arrays are finding many and varied applications from the present use in flat video displays to potential uses in microwave devices, and spacecraft charge dissipation and propulsion systems. Many of these proposed uses would require high currents per tip and operation in adverse vacuum conditions. These requirements necessitate robust cathode materials. Our work focuses on the use of transition metal carbides for field emission sources. Here, we report on vapor deposition of zirconium carbide emitter cones in the conventional field emission array geometry. Generally, we have used array blanks provided by others with 50,000 gates. We deposit these carbide emitters via physical vapor deposition from crystalline zirconium carbide sources. Use of this material has required changes in the array fabricating technique used by others due to the high temperature needed for evaporation. We will report on results of studies using several new materials for the lift-off layer and the processing steps needed for proper cone formation using zirconium carbide. The emission properties of arrays formed in this was will also be reported. In general, zirconium carbide has an electronic work function approximately 1 eV lower than molybdenum, a common FEA emitter material. This has translated into a measured lowering of turn-on voltages by 45% and an increase in emission stability. Extraction voltages in the 35-65 volt range are reported for solid carbide emitter cones in the FEA geometry. Emission at relatively high individual tip currents and at poor vacuum levels will also presented and discussed. These carbide cone arrays could lead to extremely robust electron sources and open the use of FEAs to a variety of applications. Work supported in part by DARPA High Definition Systems Initiative under ONR Grant No. N00014-96-1-1011.

9:20am **FP-TuM4 High-Speed Assembly of Flexible Film LCDs: Materials and Process Development**, *J.T. Richard,* Polaroid Corp.; ***W.K. Smyth***, Polaroid Corp., U.S. **INVITED**

Thin, flexible displays have long been considered ideal for portable display applications where weight, ruggedness and product packaging are critical performance criterion. Materials research and display assembly process development targeting flexible displays have resulted in low volume plastic display production using new materials on typical LCD production lines with comparable throughput. In order for flexible displays to become pervasive in the portable applications, new materials, equipment and processes which take advantage of high speed and low cost web assembly techniques will be required. As part of ongoing optical films research at Polaroid, new materials and processes have been developed which improve the performance of flexible displays as well as increase the potential throughput of production volume display manufacturing. A conductor film has been developed which incorporates a high temperature, low birefringence substrate and hard-coat with a thin film optical structure. The unique structure of the sputtered layers integrates high optical transmission, high electrical conductivity, and the ability to be directly patterned with commercially available, IR laser patterning equipment. This thin, durable film can be patterned in continuous rolls to enable web based display assembly. Conventional display assembly processes for edge seal and alignment layer curing and vacuum filling of liquid crystal have prohibitively long cycle times to be feasible for roll to roll display assembly. Fast curing edge seal adhesive and process conditions suitable for web based coating and drying of alignment layers have been developed. In addition, a novel display assembly process, which eliminates the need for vacuum filling, has been demonstrated.

10:00am **FP-TuM6 Growth of ITO and SiN@sub x@ Films on Polymeric Substrates For Flexible Displays**, ***P.F. Carcia***, *R.S. McLean, M.H. Reilly,* DuPont Central Research and Development

The discovery that classes of polymeric materials are electro-luminescent and the rapid progress in their development into a technology promise a revolution in future flat panel displays. Currently, the first devices are being manufactured on glass substrates. If, however, devices could be made on flexible polymeric substrates in a reel-to-reel process, this would reduce cost, improve ruggedness, and reduce weight. However, to achieve success on plastic substrates, barrier coatings are needed to exclude atmospheric gases that chemically degrade device performance, and low resistance transparent coatings are needed for efficient electro-optical performance. In this paper we investigate the relationship of the polymeric substrate and its surface morphology to the properties and structure of inorganic thin films, as examined by atomic force microscopy. Conducting ITO films were grown by rf magnetron sputtering and SiN@sub x@ films by both rf magnetron sputtering and ECR PECVD. ITO films had very small grain size, as deposited on unheated PET and PEN polymeric substrates, 2 mils thick , with sheet resistance of only about 15 ohms/square. These films were relatively thin (150-200 nm thick) with low stress and high optical transparency in the visible, and they were also surprisingly good barriers to oxygen transport. Because of their higher optical transparency, SiN@sub x@ films are more attractive in flexible polymer display devices as barriers for atmospheric gases. And SiN@sub x@ films 50 nm thick, synthesized by ECR PECVD on PET and PEN film, were excellent barriers (<0.005 cc/m@super 2@/day-atm) to atmospheric gases. Finally, we will discuss a simple method to semi-quantitatively image defects in barrier films.

10:20am **FP-TuM7 Transparent and Conductive Ultra-barrier Coatings for Flexible Plastic Displays**, ***C.I. Bright***, Delta V Technologies

One of the major issues limiting fabrication and lifetime of flexible displays is the moisture and oxygen permeability of the polymeric substrates. The acceptable value of permeation depends on the sensitivity of the particular display technology. Another flexible displays issue is the low temperature capability of optical quality plastic substrates. This restriction on process temperatures has many implications in display fabrication. One example is the low conductivity of the Transparent Conductive Oxide (TCO) used for the necessary transparent electrode layer. An organic layer deposited by the Polymer MultiLayer (PML) process for vacuum evaporation of organic monomers and in-situ e-beam or UV polymerization has demonstrated excellent smoothing of substrate surfaces. When dielectric layers of Al@sub 2@O@sub 3@ or SiO@sub 2@ are combined with PML deposited organic polymer layers; outstanding barrier properties are achieved on flexible plastic film substrates. A PML base coat layer also should provide a clean smooth surface for bonding and nucleation of a deposited TCO. In this work, we combined a PML base coat and a TCO layer to form a transparent conductive barrier where the TCO functions as both the moisture and oxygen barrier, and the required transparent electrode for the display. Multiple pairs of polymer/TCO layers can be used to increase both barrier performance and conductivity, as needed, for a particular display technology. The experimental results for ITO sputtered directly onto a PET substrate, and with a PML acrylic base coat, in a roll-to-roll (web) coating process are reported. The optical, electrical and barrier properties for both constructions were measured and compared. Very preliminary barrier results show permeation values of 0.05 - 0.005 O@sub 2@ cc/m@super 2@/day, H@sub 2@O g/m@super 2@/day, for single layer ITO on a PET (0.007" thick) substrate.

10:40am **FP-TuM8 Fabrication of OLED Devices on Flexible, Ultra-barrier Plastic Substrates***, **G.L. Graff**, M.E. Gross, P.A. Mounier, M.K. Shi, M.G. Hall,* Battelle Pacific Northwest National Laboratory*; J.J. Brown, J.K. Mahon,* Universal Display Corporation*; C.I. Bright,* Delta V Technologies*; P.E. Burrows,* Princeton University

To develop displays on flexible polymeric film substrates, transparent ultra-barriers to oxygen and moisture must be provided. The acceptable value of permeation will depend on the sensitivity of the particular display technology. A multilayer film structure with alternate layers of organic polymer and metal oxide, has demonstrated oxygen and moisture permeation rates below the measurement limit of commercial instrumentation (<0.005 O2 cc/m2/day, H2O g/m2/day). This highly transparent, multilayer ultra-barrier coating was deposited by roll-to-roll compatible, vacuum deposition processes. The Polymer MultiLayer (PML) process for vacuum evaporation of organic monomers and in-situ polymerization, was used to deposit the organic layers. DC reactive magnetron sputtering was used to produce the aluminum oxide barrier layers. A transparent conductive coating of ITO was sputter deposited over these ultra-barrier layers to provide a transparent electrode for display construction. Typical performance for a 135 nm thick ITO layer, deposited on a double hardcoated PET (7 mil thick) substrate with ultra-barrier layers, was = 85%T and = 70 ohms/square. OLED devices have been fabricated using the flexible, ultra-barrier substrates, and preliminary device performance will be reported.

11:00am **FP-TuM9 Photoisomerization and Photo-induced Alignment of Azobenzene Containing Dyes and Polymers in Ultrathin Films Fabricated by the Alternate Polyelectrolyte Deposition (APD): Application for LC Displays***, R.C. Advincula,* University of Alabama at Birmingham, US*; **M.-K. Park**,* University of Alabama at Birmingham*; A. Baba, F. Kaneko,* Niigata University, Japan

The incorporation of a photochromic moiety in polymers is very attractive due to the possibility of creating new light-sensitive materials and optical devices. Ultrathin films containing photoisomerizable moieties, e.g. azo dyes are excellent materials for inducing control in LC molecules (command layer effects), holographic surface relief gratings, optical storage media, nanoscale applications, etc. In this work we have employed the alternate polyelectrolyte deposition (APD) on solid substrates to fabricate ultrathin films containing photoactive azobenzene groups. We investigated the combination of polymer containing azobenzene dye (PAZO)/ polycation (PDADMAC or PDDA) system and the small molecule dye Direct Red 80/PDADMAC system at various layer thicknesses. The uniform layer by layer assembly of the films was determined by UV-vis spectroscopy, ellipsometry, X-ray reflectivity, QCM, AFM, and SPS. The complex photoisomerization behavior reveals the importance of layer ordering, azobenzene mobility, and aggregation states in determining the future utility of these films. We utilized polarized UV-light to induce photoisomerization and photo-alignment of these ultrathin films. Hybrid LC Cells reveal in-plane homogeneous alignment. Correlation was made on the effect of film formation parameters to the overall film quality and layer ordering. We observed high anisotropies dependent on the dye, layer preparation, thickness, etc. LC Cells made from 5 CB reveal read/write capabilities dependent on the thickness and irradiation parameters. Future possibilities for LC and Large area display device modifications are envisioned.

11:20am **FP-TuM10 Plastic Liquid Crystal Displays from Conducting Polymer***, **R. Shashidhar**,* Naval Research Laboratory*; L. Huang, C. O'Ferrall,* Geo-Centers Inc./Naval Research Laboratory*; W. Fritz, J. Doane,* Liquid Crystal Institute **INVITED**

In a conventional liquid crystal display device (LCD), glass substrates coated with an indium tin oxide (ITO) layer are typically used for the application of an electric field to the liquid crystal material. For many applications, there is a need for a LCD with a plastic substrate. Polypyrrole is a well known conducting polymer for its high conductivity and chemical stability. Compared with the currently used ITO conducting layer, polypyrrole is more compatible mechanically with plastic. Because it is an organic material, it should be able to bend and flex with the substrate. Here we describe the preparation of polypyrrole films on a polyethylene terephthalate (PET) substrate by an in-situ solution deposition process and their patterning by conventional photolithography techniques. We will discuss their important physical properties, such as surface resistance and optical transmission and their suitability as a substitute for ITO as an electrode for a plastic reflective Cholesteric reflective LCD. We have demonstrated for the first time the operation of a fully multiplexed plastic (LCD) using conducting polymers (on plastic) as the substrates and the reflective cholesteric display technology. The resultant display has several features like lightweight, low power consumption, increased ruggedness, bistability, sunlight readability and flicker-free operation. The functioning of the conducting polymer-based LCD is demonstrated and the features that make it attractive for many applications are discussed.

Magnetic Interfaces and Nanostructures Technical Group
Room 618/619 - Session MI+VM+AS-TuM

Magnetic Recording: Media

Moderator: H.T. Hardner, Seagate Technology

8:20am **MI+VM+AS-TuM1 Perpendicular Patterned Media: Fabrication and Demonstration of Data Storage***, **J. Wong**[1], A. Scherer,* California Institute of Technology*; M. Todorovic, S. Schultz,* University of California, San Diego

Patterned media has been proposed as one of the solutions to extending data storage densities beyond 100Gbits/in@super 2@. We have fabricated perpendicular patterned media using a combination of high resolution electron beam lithography, dry etching, and electroplating. Futhermore, we have successfully demonstrated data storage in such structures. We first use vector scanned electron beam lithography to define the dot array pattern on the PMMA coated Al@sub 0.9@Ga@sub 0.1@As/GaAs substrate. After development, this pattern is transferred into the substrate using Chemically Assisted Ion Beam Etching (CAIBE). Immediately following CAIBE, we convert the Al@sub 0.9@Ga@sub 0.1@As layer into (Al@sub 0.9@Ga@sub 0.1@)@sub 2@O@sub 3@ using wet thermal oxidation. We take advantage of the highly selective etching properties of GaAs and the durable masking properties of (Al@sub 0.9@Ga@sub 0.1@)@sub 2@O@sub 3@ to create high aspect ratio Ni columns. After the dot arrays are defined in the substrate, we use electroplating to fill the etched holes with Ni, followed by polishing.@footnote 1@ Using Magnetic Force Microscopy, we find that the Ni columns are stable single domain magnets. We demonstrate data storage in these structures by controllably orienting the magnetization of individual 170nm diameter Ni columns using conventional thin film write poles. We subsequently read back the stored information using current MR or GMR read heads.@footnote 2@ This demonstration bridges the gap between the fabrication of such structures and their use in actual magnetic storage systems. Work is in progress to characterize higher density arrays (~1.3, 2.6, and 5.2Gbits/in@super 2@) in the form of data tracks (1µm in the x-direction and 0.5, 0.25, and 0.125µm apart respectively in the y-direction). @FootnoteText@ @footnote 1@ J. Wong et al., J. Appl. Phys. 85, 5489, 1999. @footnote 2@ M. Todorovic et al., Appl. Phys. Lett. 74, 2516, 1999.

8:40am **MI+VM+AS-TuM2 Ion Beam Patterning of Magnetic Recording Media With a Stencil Mask***, **B.D. Terris**, L. Folks, D. Weller, J.E.E. Baglin, A.J. Kellock,* IBM Almaden Research Center*; H. Rothuizen,* IBM Zurich Research Lab*; P. Vettiger,* IBM Zurich Research Lab, Switzerland

In conventional scaling of magnetic recording media, the grain size is reduced as the bit density is increased, while the number of grains per bit is held approximately constant to maintain signal to noise levels. This scaling approach, however, will reach a fundamental limit when the grain sizes become so small that they are subject to reversal due to thermal excitation on time scales of less than the required data retention time. One approach to circumventing this thermal limit is to create magnetic bits that behave as single magnetic entities, e.g. either single domains or a collection of strongly coupled grains, rather than the hundreds of weakly coupled grains per bit found in conventional granular recording media. In one approach to patterned media, ion beam irradiation is used to locally alter the magnetic properties of thin Co/Pt multilayer films.@footnote 1@ With sufficient ion dose, the easy axis of magnetization is rotated from out-of-plane to in-

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[1] **Falicov Student Award Finalist**

plane. We have used this process in conjunction with a silicon stencil mask having 1 micrometer diameter holes to pattern regularly spaced micrometer-sized regions of magnetically altered material over areas of a square millimeter. The nature of these magnetic structures has been investigated by magnetic force microscopy. The technique is demonstrated with mask-sample spacing as large as 0.5 mm. In addition, smaller regions of magnetic contrast, down to 100 nm, were created by using two masks with partially overlapping micrometer holes. Unlike other patterning techniques, this approach is non-contact and does not require post-processing to clean the disk, both potential manufacturing advantages. @FootnoteText@ @footnote 1@ C. Chappert et al., Science 280,1919(1998).

9:00am **MI+VM+AS-TuM3 Ion Induced Magnetization Reorientation in Co/Pt Multilayers for Patterned Media*, D. Weller,*** *J.E.E. Baglin, K.A. Hannibal, M.F. Toney, L. Folks, A.J. Kellock, M.E. Best, B.D. Terris,* IBM Almaden Research Center

Ion beam patterning of magnetic thin films using stencil masks is a prospective path towards ultrahigh-density magnetic recording media. Co/Pt multilayers are ideally suited for this application, since they undergo a spin-reorientation transition from easy axis out-of-plane to easy axis in-plane upon irradiation with ions of suitable energy and dose.@footnote 1@ The mechanism, leading to the observed modulation in magnetic properties is of great fundamental and technological interest and will be discussed in this paper. Electron beam deposited Co/Pt multilayers with representative structure [Si-substrate/SiNx/20 nm Pt buffer/10x(0.3nm Co/1 nm Pt)/2 nm Pt cap layer] were used. These structures have high coercivity (H@sub C@ = 5000- 8500 Oe) and exhibit square perpendicular hysteresis. The high coercivity is attributed to the the large perpendicular anisotropy (K@sub u@ = 4.3 10@super 7@ erg/cm@super 3@) and granularity of these films as indicated in AFM surface topography measurements. The structures were subjected to various doses and currents of 700 keV N@super +@ ions and investigated after each irradiation step using grazing incidence X-ray reflectivity and Kerr hysteresis loop measurements. Direct evidence for ion beam mixing at the Co/Pt interface is found from the XRD data. In particular, we find an almost linear decrease of the integrated intensity of the first grazing incidence Bragg peak with ion dose. This correlates with the measured remanence ratio and anisotropy, however, not with the coercivity, which drops off much faster. @FootnoteText@ @footnote 1@ C. Chappert et al., Science 280, 1919 (1998).

9:20am **MI+VM+AS-TuM4 Texture and Strain in Cr/NiAl Films Grown on Glass Substrates*, G. Khanna*[1]**, *B.M. Clemens,* Stanford University

Glass has recently emerged as a promising candidate to replace NiP/Al in magnetic recording media due to its smooth surface and high shock resistance. A NiAl seed layer may be employed to produce the desired (112) orientation in the Cr underlayer and a (1010) orientation in the Co-alloy magnetic layer. Since NiAl forms the template for subsequent growth of Cr and Co, determining its growth texture and strain is critical to understanding the microstructure and magnetic properties of the media. We report on synchrotron radiation experiments on Cr/NiAl films of various thicknesses grown on glass substrates at elevated temperatures. Our results demonstrate that the growth of the NiAl (and consequently the Cr) on glass substrates is markedly different from Cr growth on traditional Al/NiP substrates. While a strong (002) out-of-plane texture develops at elevated temperatures in the latter case, no particular growth orientation dominates in the NiAl. Both (110) and (112) reflections appear out-of-plane in Cr films grown on thin seed layers. This result indicates that both growth orientations are present in the NiAl since the Cr grows epitaxially on the NiAl surface. Furthermore, several out-of-plane reflections appear in thick NiAl films which implies that, initially, there is simultaneous growth of NiAl grains having several different orientations. Integrated intensities of (110) reflections suggest that NiAl (110) grains are overgrown as the film thickness increases. A comparison of pole figures shows that the NiAl (110) peak is shifted to @Delta@ @psi@ = 30 from the out-of-plane direction for thicker films. The evolution of the texture with depth may be quantified using grazing incidence geometry and varying the incident angle. Intensity ratios from GIXS in-plane reflections corresponding to particular out-of-plane orientations are used to depth profile the texture. The in-plane reflections may also be used to determine the inhomogeneous strain in both layers.

9:40am **MI+VM+AS-TuM5 Ultrafast Magnetization Dynamics in Magnetic Thin Films*, T.M. Crawford,*** Seagate Research **INVITED**

If one extrapolates the current growth trends for disc drive data rates, the data rate expected by the year 2005 is 2.4 Gbits/sec, requiring magnetization reversal frequencies in the GHz range. However, Permalloy (NiFe), a standard material used for inductive write heads, exhibits ferromagnetic resonance (FMR) at ~ 630 MHz, which is a 10%-90%, precession-limited switching time of 550 ps. While increasing the saturation magnetization and/or anisotropy shifts this resonance to higher frequencies, the gain in switching speed is proportional to only the square root of such increases. As a result, operating magnetic recording heads at or near the FMR frequency may be a necessity to achieve the desired data rates in future storage devices. This rapid increase in data rate toward the fundamental switching speed limit has generated renewed interest in the field of high speed magnetic switching and magnetodynamics, originally studied extensively in the 1950's and 1960's. This renewal has been assisted by the availability of faster electronic and optical techniques with improved signal-to-noise for characterizing magnetic materials and devices at times well below 1 ns. Recent contributions to this field in the form of time-domain switching measurements, where the film magnetization is driven far from equilibrium, will be reviewed. Subtle material-dependent phenomena which have been observed by these techniques, including possible differences in bulk and surface magnetic properties, will be discussed, as will the possibility of actively controlling the magnetodynamics to achieve a desired behavior. Finally, the extension of these techniques to more complicated materials systems and nanoscale device structures will be addressed.

10:20am **MI+VM+AS-TuM7 Temperature Dependent Characterization of Thermal Stability of Longitudinal Magnetic Recording Media*, A. Moser,*** *D. Weller, E. Fullerton, K. Takano,* IBM Almaden Research Center

Temperature dependent characterization of thermal stability was performed on a series of magnetic recording media at temperatures between 300 K and 420 K using a static write/read tester.@footnote 1@ The investigated samples are CoPtCr alloys with thicknesses in the range between 5.5 nm to 13 nm. First, the thermal stability of a recorded bit track was studied by measuring the time-dependence of the read-back amplitude between 0.8 s and 70000 s. Second, the time-dependent coercivity was measured by applying a magnetic field pulse of 5 ns to > 60 s width opposite to the sample's initial magnetization. Finally, the samples were characterized by SQUID magnetometry yielding temperature dependent coercivities, viscosity parameters and irreversible susceptibilities. The measurements are discussed with a quasi-independent particle model. The measured stability ratios (ratio between energy barrier for magnetization reversal to thermal energy) and signal decay rates are found to decrease faster than simple scaling with temperature would predict. @FootnoteText@ @footnote 1@ A. Moser, D. Weller and M.E. Best, J. Appl. Phys. 85, 5018 (1999)

10:40am **MI+VM+AS-TuM8 High Resolution FE-Auger Electron Spectroscopy: Applications in Magnetic Recording, Heads and Media*, C.A. Fenno,*** Seagate Technology - Colorado Design Center

As the Disk Drive Industry pushes toward higher capacity, smaller form factors, and better performance, head and disc design has changed considerably. Technological advances have resulted in decreased dimensions; thinner layers on the disc and within the head reader element, and lower flight heights. As a result the tools used in material characterization requires improved spatial resolution, increased depth resolution and increased spectral resolution. One answer to the challenge of evaluation and characterization of smaller disc and head features is FE-Auger Electron Spectroscopy. FE-Auger provides elemental analysis with excellent spatial resolution. In the best case the electron spot size can achieve 20nm although in the practical case on disc and head features an electron spot size of 60-100nm is more typical. Features of sub-micron dimensions are routinely analyzed with FE-Auger. In some cases high spectral resolution FE-Auger data can reveal chemistry as in the case of titanium-, silicon-, and aluminum-based particles as well as in the case of some oxides and carbides. This chemical data is obtained from particular energy shifts or peak shape change from the respective materials. This presentation will show several examples where the high spatial and spectral resolution available with FE-Auger was instrumental in diagnoses in drive failure analysis.

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[1] **Falicov Student Award Finalist**

11:00am **MI+VM+AS-TuM9 Characterization of Co/CN@sub x@ Granular Media Prepared by Nanolamination**, *C. Ruby, J. Du, R. Zhou,* ***S.C. Street****, J. Barnard,* The University of Alabama

Cobalt-carbon thin films proposed for use as granular magnetic media are generally prepared by co-deposition sputtering. An alternative method is nanolamination of the component layers (media and matrix) followed by annealing. The potential advantages of this approach include precise control over component volume fractions and ease in fabricating large, uniform samples. We have produced and characterized thin film granular structures prepared from nanolaminate layers of Co and CN@sub x@. TEM studies of the microstructure indicate that for certain samples discrete domains are generated, with mean grain sizes of around 20 nm, with near lognormal distribution. These films have coercivities above 1200 Oe. Surface characterization by XPS depth profiling indicates that the annealed films have oxidized cobalt in the very near surface region, although initial study did not show any magnetic hysterisis loop shift. AFM measurements show that the surface of the film roughens significantly upon annealing, with the RMS roughness increasing from 0.2 nm to 1.0 nm. Thus, it appears that the mixing involved in the annealing process, which gives rise to grain formation, also degrades the smooth surface of the CN@sub x@ capping layer and exposes some of the cobalt to ambient. The implications of this process on tribological issues is explored.

11:20am **MI+VM+AS-TuM10 Characterization of Hard Disk Drives by Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS)**, ***B. Hagenhoff****, R. Kersting,* TASCON GmbH, Germany; *D. Rading, S. Kayser, E. Niehuis,* ION-TOF GmbH, Germany

Hard disks used in hard disk drives consist of a complex inorganic and organic layer structure. Whereas substrate near layers are inorganic of origin and can be comparatively thick, layers closer to the surface become very thin and are finally covered by an organic F containing lubricant. Defective production processes as well as normal use can change the original layer structure and composition. For an analytical characterization of these changes a technique is required which gives detailed information on the chemical composition in lateral as well in depth directions. Time-of-flight secondary ion mass spectrometry (TOF-SIMS) is ideally suited to perform this task because it offers elemental as well as molecular information with high sensitivity. A 3-D representation of the sample can be obtained by combining sputter depth profiling and imaging. With modern TOF-SIMS instruments meanwhile a lateral resolution of less than 200 nm and a depth resolution of only a few nm can be obtained. We therefore applied TOF-SIMS to the characterization of commercially available hard disks. We concentrated on the identification of the lubricant present in the uppermost monolayer, screening for corrosion spots and layer structure elucidation. Special emphasis was laid on the automation of measurement and data evaluation routines in order to enhance sample throughput for industrial applications. Examples for spectroscopy, imaging and depth profiling will be presented.

Manufacturing Science and Technology Group
Room 611 - Session MS-TuM

New Manufacturing Research Paradigms

Moderator: C.B. Whitman, CVC Products Inc.

8:20am **MS-TuM1 Proposal of New Paradigm LSI Structures and Their Manufacturing**, ***T. Ohmi****, M. Hirayama, Y. Shirai,* Tohoku University, Japan **INVITED**

UCS (Ultra Clean Society) was established in October, 1988 and is going to finish its mission at the end of September, 2000. For these 11 years, UCS has developed many new technologies mainly focussing on an improvement of process quality by removing unknown factors from manufacturing such as contaminants (particles, metals, organic molecules, moisture molecules, native oxides, surface micro-roughness, electrostatic charge-up and etc.) and fluctuations of process parameters giving an influence on process results. Consequently, semiconductor processes can be understood in a scientific manner, resulting in an improvement of process reproducibility. Developments of very well regulated high density plasma source for RIE, sputtering and plasma CVD, and room temperature 4 steps substrate surface cleaning have drastically improved process quality and process reproducibility. Equipment individuality has been overcame by introducing RF circuit specification to the process chamber and very well regulated process gas supply to the wafer surface by newly developed Flow Control System, so that so that process recipe can be applied to all other identical process chambers resulting in a complete process reproducibility and a low price process equipment. Right now, very high throughput and very compact manufacturing line must be established having a capability of simplified process steps, very low consumption volume of electricity and resource materials down to 1/10. Complete process reproducibility will make it true the computer simulation of all processes by microprocessors. Process flow and process conditions will be derived by computer simulation just after the completion of LSI design. Manufacturing of newly designed LSI will start immediately without using pilot wafers. Very low cost and very QTAT manufacturing are crucial for coming networked digital home electronics era. New society will focus on these issues.

9:00am **MS-TuM3 The IC Interconnect Millenium Transitions; Al to Cu, SiO@sub 2@ to Low-K**, ***K.A. Monnig****, A.C. Diebold,* SEMATECH **INVITED**

This paper will give a general overview of the transitions occurring in I.C. interconnect systems today; Al conductors with SiO@sub 2@ insulators are planned to be supplanted by Cu metal with Low-K dielectrics. The reasons why this transition is happening now will be outlined. Almost all of the fabrication processes used will be changed and these differences will be reviewed. Special attention will be given to vacuum processing applications that will be lost due to the changes and to the new opportunities created. An assessment of financial and technical risks will be shown. Finally a current status report on the progress of the various transitions will be presented.

9:40am **MS-TuM5 Cooperative University Research for Critical Front End IC Processes**, ***J.R. Hauser****,* North Carolina State University **INVITED**

MOS device physics and technology are rapidly approaching some fundamental limits as device dimensions are scaled below 100 nm. Fundamental tunneling limits to SiO2 gate oxide are approaching as oxide thickness scales below 2 nm. Low resistance source/drain contacts are becoming increasingly difficult as junction depths decrease and required doping densities approach or exceed solid solubility limits. In order to address these issues, a new cooperative research center was established in 1998, the SRC/SEMATECH Front End Processes Research Center. The Center seeks to bring together research in three areas: (a) Fundamental materials and interface physics and chemistry, (b) Process integration and demonstration and (c) Rapid transfer of technology to industry and equipment companies. To effectively integrate such research efforts, requires new paradigms for cooperative university research and this presentation will discuss how this is being approached within the SRC/SEMATECH Research Center.

10:20am **MS-TuM7 Industrial-Academic-Government Partnerships; A Successful Example**, ***J.B. Bindell****,* Cirent Semiconductor (Lucent Technologies) **INVITED**

Semiconductor manufacturers have always had a close relationship to Universities, using them for purposes ranging from professional training to contract research and development. These relationships have also been synergistic, with the Universities strongly benefiting from in depth relationships with high technology firms. These reverse benefits have also been multifaceted, with funding, training delivery opportunities and contact with well known industrial scientists yielding many productive interactions. When Lucent Technologies located its leading edge manufacturing facility in Orlando, Florida, and then moved a major Bell Labs R&D division to the same facility, a number of interactions were suddenly spawned. Three distinct players were involved. These were Lucent, which found itself in need of strong University support, the University of Central Florida (UCF) and the University of South Florida (USF), both relatively close neighbors, and the state of Florida itself which had designated an extended area between Orlando and Tampa as the "Florida High Tech Corridor". The corridor's establishment was an important part of a desire to make this region a magnet for additional semiconductor manufacturers and for the economic growth that would surely follow. This three-way partnership between industry, government and education has led to a new paradigm for such interactions in which the boundary between our industrial laboratory and those of the Universities has become unclear. In fact, in the disciplines where Lucent has needed University support, these partnerships have created resources which are well on their way to national prominence. This presentation will center on the University programs and facilities that have developed from this partnership as well as on the issues of industrial involvement in the area of workforce development.

11:00am **MS-TuM9 Cooperative Research on Environmentally Benign Semiconductor Manufacturing**, ***F. Shadman,*** NSF/SRC Engineering Research Center **INVITED**

This presentation will be an overview of the multi-disciplinary research program at the NSF/SRC Engineering Research Center involving a team of researchers from six universities. The Center is focusing on a dual approach to the environmentally benign semiconductor manufacturing. The first approach involves the development of novel processes where environmental, safety, and health (ESH) factors are among the primary design parameters together with performance and cost. The second approach focuses on improving the existing processes for ESH gain. Several examples of the thrust areas and projects of the Center will be discussed. In particular, the following topics will be covered in depth: Reduction of water and chemical usage for surface preparation and wafer cleaning; Environmental gains in the development of new low-k materials/processes as well as the new etch and deposition methods; Waste reduction and recycling in the CMP process; Energy use reduction through novel purification processes; Application of simulation and integrated modeling for recycle and reuse optimization in selected fab processes. Finally, the educational program of the Center that focuses on including the ESH subject in the core engineering curriculum will be discussed briefly.

11:40am **MS-TuM11 EquiPSim: Hands-On Training in Semiconductor Equipment and Process Behavior**, *A.R. Rose,* ***G.W. Rubloff****, N. Kositsyna, N. Gupta, R. Sreenivasan, W.S. Levine,* University of Maryland

We have developed EquiPSim (Equipment and Process Simulation), a software-based learning system for semiconductor manufacturing aimed at providing active hands-on experience in the equipment and process environment of semiconductor manufacturing. Physically-based dynamic simulators, validated against experiment, were constructed on a commercial PC-based simulation software platform (VisSim@super TM@ v/3) and linked to a graphical user interface built on a Delphi@super TM@ v/4 visual development platform. As the learner operates the controls (actuators such as valves, settings, etc.) on the equipment or changes system design variables, system responds realistically and accurately in real time, allowing the user to explore system behavior freely and to carry out open-ended learning exercises. A host of user-controllable tools are also provided to present a rich learning environment, including: guidance, reference, and exercise materials in hypertext, accessed locally or over the Internet; active links between the guidance materials and the visual representation of the system; tools for modifying system design parameters; a lab notebook for recording design parameter and experimental results; and tools to enable distance collaboration. The software architecture is structured to facilitate separable authoring, in which the domain expert need concentrate only on the physical fidelity of the simulator and the guidance concepts to be taught, while the user interface is built from templates and predefined application objects by someone with modest software skills. Modules covering vacuum and gas flow technology, heat transfer mechanisms, and chemical reaction processes are aimed at novices, while modules in process control and optimization strategies are aimed at more experienced learners. The presentation will feature a live demonstration. Further information is available at the Center for Engineered Learning Systems (CELS) website at /www.isr.umd.edu/CELS/.

Nanometer-scale Science and Technology Division
Room 612 - Session NS1-TuM

Nanomechanics

Moderator: B. Unertl, University of Maine

8:20am **NS1-TuM1 A Progress Report on the Road to Quantitative Nanotribology**, ***R.W. Carpick,*** Sandia National Laboratories **INVITED**

The goal of routinely acquiring reliable, quantitative nanomechanical and nanotribological measurements with scanning force microscopy (SFM) has not yet been reached. As we travel along the exciting road toward this goal, several signposts warning us of the complications and drawbacks of SFM techniques have been recorded. In this talk I will discuss the current state of affairs regarding accurate measurement of mechanical and tribological properties at the nanometer scale. The critical roles of force calibration, tip characterization, cantilever properties and accurate displacement control will be discussed. Particular attention will be paid to the case of normal and lateral force measurements with contact-mode SFM. I will investigate the application of continuum mechanics models to SFM measurements, including recent models relating fracture mechanics and sliding friction measurements. Finally, I will discuss advantages gained by using novel instrumental approaches. * Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract DE-AC04-94AL85000.

9:00am **NS1-TuM3 Contact Properties of Oxide Surfaces: Long Range Forces and Adhesion**, ***E. Barthel****, A.S. Huguet, R. Roquigny, S. Sounilhac,* CNRS / Saint Gobain Recherche, France **INVITED**

Surface Forces Microscopy (SFM) is useful to caracterize adhesive properties of surfaces. In practice, however, the usual relations between pull-off force and adhesion energy (JKR, DMT) may sometimes be inadequate, because the assumptions inherent to these models are not fulfilled. Using a general approach to the adhesive contact problem, based on Sneddon's results, and specific descriptions of the interaction(s) relevant to the cases under study, we will consider three non-trivial cases: 1) Silica/silica contact: in this case, both very short-range and long-range interactions contribute. We show how to split the total adhesion energy into its long-range and short-range contributions.@footnote 1@ 2) Surfactant monolayers: recent experiments@footnote 2@ have evidenced a power law dependance of the pull-off force as a function of driving velocity when surfactant monolayers are deposited on the surfaces. We provide an analytical model for this case, where viscoelastic losses are essential 3) Metal/oxide contact: using an UHV AFM, we have investigated the tungsten/oxide adhesion and long range forces.@footnote 3@ Short-range forces are shown to form the main contribution, although we did not achieve quantitative assesment. CONCLUSION Surface Forces measurements are a versatile tool for understanding interaction and adhesion properties of oxide surfaces. However, the bare pull-off force may reflect a variety of phenomena, which have to be properly taken into account in the data treatment. @FootnoteText@ @footnote 1@ Barthel E., Colloids and Surfaces A, 1999, 149, 99. @footnote 2@ Ruth M. and Granick S., Langmuir, 1998, 14, 1804. @footnote 3@ Sounilhac S., Barthel E. and Creuzet F., J. Appl. Phys., 1999, 85, 222.

9:40am **NS1-TuM5 Metallic Adhesion and Tunneling at the Atomic Scale**, ***A. Schirmeisen****, G. Cross, A. Stalder, P. Grutter,* McGill University, Canada; *U. Durig,* IBM Research Division, Zurich Research Laboratory

We have measured forces and currents between atomically defined W(111) tips and a Au(111) sample in ultra high vacuum at 150 K. The W tips are manipulated and characterized on an atomic scale both before and after the experiment by field ion microscopy (FIM). The force-distance curve shows a peak of the attractive, adhesive metallic force of 5 nN for a three atom tip. Unexpected for a metallic system, there is no spontaneous jump-to-contact (Cross et al., PRL 80. 4685 (1998)). An analysis of the tip by FIM after the approach reveals an atomically unchanged tip apex even for repulsive forces of up to several nN. From a fit of our data to the Maugis-Dugdale theory we can determine that our system is close to the rigid body Bradley limit. The experimental data is described very well with a scaled Rydberg function with an unexpected large decay length of 0.2 nm. The simultaneously measured tunneling current has the expected exponential dependence on tip-sample separation, giving a reasonable barrier height of 3.7 eV. After a model proposed by Chen (J. Phys. Cond. Mat 3, 1227 (1991)) there should be a direct correlation between the tunneling current and adhesion force. Using our experimental data we extract a value for the LDOS of the W trimer tip of 1 state/eV/atom at the Fermi energy, which is in agreement with theoretical predictions. Finally, we have measured the evolution of the tip-sample contact for a tip radius of 3 nm and repulsive loadings as large as 200 nN. Half of these measurements show little or no hysteresis, whereas in the remaining indications of reversible slip behavior was observed.

10:20am **NS1-TuM7 Interphase Nanomechanical Properties in a Model Epoxy-Silane-Glass Composite as Revealed by Interfacial Force Microscopy**, *H. Cabibil, J.M. White,* University of Texas, Austin; *J.E. Houston,* Sandia National Laboratories; ***R.M. Winter,*** S.D. School of Mines and Technology

The interfacial force microscope (IFM), a scanning probe microscope utilizing a self-balancing differential capacitance force sensor, was used to measure directly the interphase elastic and visco-elastic properties in model epoxy-silane-glass systems. Model composites were fabricated from diglycidyl ether of bisphenol F, diethyltoluenediamine and gamma-aminopropyltrimethoxysilane; an epoxy, amine curing agent, and organosilane respectively and optical silica fibers as the reinforcement and chemical sensor. The elastic modulus was determined directly from the force profiles using a contact mechanics analysis. It was found that the elastic modulus varies significantly with respect to the bulk in a 1-5 micron region surrounding the 50 micron glass fibers. The relaxation and creep response of the interphase was probed to investigate the visco-elastic response of the interphase. An organosilane-epoxy-glass system was also developed to model the interphase region and was probed with the IFM. Visco-elastic analysis of the model interphase yields storage and loss moduli. Fourier transform infrared evanescent wave spectroscopy, utilizing the fibers or a parallelepiped (the model interphase substrate) as both a waveguide and an evanescent sensor, and x-ray photoelectron spectroscopy were used to characterize the bulk and interphase chemistry of the systems. The relationship between interphase chemistry and nanomechanical properties were examined and will be discussed. The portion of this work done at Sandia, which is a multiprogram laboratory operated by Sandia Corporation - a Lockheed Martin Company, was supported by the United States Department of Energy under Contract DE-AC04-94AL85000.

10:40am **NS1-TuM8 Nanoindentation Mechanism and Surface Recovery in an Ionic Crystal Surface, MgO(100)***, **P.F.M. Teran Arce**, G. Andreu Riera, P. Gorostiza, F. Sanz,* Universidad de Barcelona, Spain

The atomic force microscope can be used to perform nanoindentations on surfaces. With the resulting indentation curves one is enabled to characterize at the nanometer level elastic and strength properties of materials. Furthermore, one is allowed to follow in situ the recovery of the surface after the indentation, therefore gaining insight into the processes affecting the dynamical behavior of the surface. We have carried out nanoindentations, only a few monatomic layers deep, on a semibrittle surface, MgO(100), utilizing an atomic force microscope both for indenting and imaging. Indentations were performed by scanning the piezo vertically until the tip contacts and eventually indents the surface. A force curve was recorded to characterize in situ the indentation. It was found that relative humidity, RH, plays a fundamental role in the kinetics of surface recovery after the indentation. Therefore, in order to avoid the influence of recovery processes in the measurement of cavity dimensions, indentations were carried out at 0 % RH when measuring elastic or strength properties. The force curves obtained show characteristic discontinuities associated with atomic layers being expelled by the tip penetrating the surface. Indentation curves extracted from the force plots show clearly two regions. One of them corresponds to the elastic deformation of the crystal. The other one starts with the onset of discontinuities and corresponds to plastic deformation. The Young modulus and hardness values of MgO(100) obtained from these experiments agree well with the known macroscopic values.

11:00am **NS1-TuM9 The Formation and Evolution of Pileup in Nanoscale Contacts***, **K.F. Jarausch**,* North Carolina State University*; J.D. Kiely, J.E. Houston,* Sandia National Laboratories*; P.E. Russell,* North Carolina State University

The interfacial force microscope (IFM) was used to indent and image defect free Au surfaces, providing atomic-scale experimental observations of the onset of pileup. The images and load-displacement measurements demonstrate that elastic accommodation of an indenter is followed by two stages of plasticity. The initial stage is identified by slight deviations of the load-displacement relationship from the predicted elastic response. Images acquired after indentations showing only this first stage of plasticity indicate that these slight load-relaxation events result in permanent deformations 0.25 to 4.0 nm deep with no evidence of pileup or orientation dependence. The second stage is marked by a series of dramatic load-relaxation events and permanent deformations 10-100+ nm deep. Images acquired following this second stage document 0.25 nm high pileup terraces which reflect the crystallography of the surface as well as the indenter geometry. Attempts to plastically displace the indenter 4-10 nm deep into the Au surface were unsuccessful, demonstrating that the transition from stage one to stage two plasticity is associated with overcoming some sort of barrier. Stage one plasticity is consistent with previously reported models of dislocation nucleation. The dramatic load relaxations of stage two plasticity, and the pileup of material above the surface, require cross-slip and appear to reflect a dynamic process leading to dislocation intersection with the surface. The IFM measurements reported here offer new insight into the nucleation, structure and evolution of the dislocations associated with the very early stages of plasticity. This work was supported by the United States Department of Energy under Sandia Contract DE-AC04-94AL85000. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company.

11:20am **NS1-TuM10 Measuring and Imaging Contact Stiffness Quantitatively at the Nanoscale using Force Modulation***, **S.A. Syed Asif**,* University of Florida*; K.J. Wahl, R.J. Colton,* Naval Research Laboratory

Depth-sensing nanoindentation has been widely used to measure the nanomechanical properties of materials. However, measuring quantitative mechanical properties of surfaces and thin films on a scale below 10 nm is still a problem. In this presentation we show that combining force modulation with depth-sensing nanoindentation allows measurement of the mechanical properties of materials on the sub-nanometer scale. The stiffness sensitivity of the technique is ~0.1 N/m, which is sufficient to detect long-range surface forces and locate the surface of compliant materials. The tip-surface interaction during approach to contact, asperity deformation during contact and time-dependent deformation at the atomic scale can all be studied. We also present a novel quantitative stiffness imaging technique, which can be used directly to map the mechanical properties of materials with sub-micron lateral resolution. Quantitative stiffness imaging is particularly valuable for polymers, thin films, and other nanostructured materials.

11:40am **NS1-TuM11 SFM Studies of Environmentally Assisted Detachment of Strongly Adhering Particles@footnote 1@***, **R.F. Hariadi**, S.C. Langford, J.T. Dickinson,* Washington State University

The production of flat surfaces is often hindered by small particles that adhere strongly to the substrate. We have undertaken a model study of the detachment of sub-micron particles via tribological interactions. Scanning force microscope, silicon nitride tips (typically about 50 nm in diameter) are used to apply stress to 10-100 nm single crystal NaCl crystallites grown on and strongly bonded to soda-lime glass substrates. In most experiments, the applied force is a combination of a compressive normal force and a lateral force, both measured simultaneously. In a time- and spatially-resolved fashion, we apply the stress and measure the response (e.g., detachment). Only the smallest particles can be detached in dry air. However, as the relative humidity (RH) is increased, the crystallites detach at considerably lower stresses. We also observe particle reattachment as a function of time and RH; all reattachments show only a fraction of the original adhesion. We model the detachment process in terms of environmentally enhanced crack growth (due to moisture); when the crack reaches a critical length that depends on particle size, catastrophic interfacial fracture follows. Numerical estimates of the necessary work of adhesion, based on a network of ions interacting via polar forces with the glass, are described. These calculations are in reasonable agreement with our data. @FootnoteText@ @footnote 1@Work supported by the NSF Surface Engineering and Tribology Program under Grant CMS-98-00230.

Nanometer-scale Science and Technology Division
Room 6C - Session NS2-TuM

Molecular Electronics

Moderator: R.J. Hamers, University of Wisconsin, Madison

8:20am **NS2-TuM1 Single Molecule Engineering: Synthesis of Individual Biphenyl Molecules on Cu (111) with STM Tip***, **S.W. Hla**,* Freie Universitat Berlin, Germany*; L. Bartels,* Columbia University*; G. Meyer, K.-H. Rieder,* Freie Universitat Berlin, Germany

In 1904, Fritz Ullmann et al. discovered the way to produce biphenyl from iodobenzene by using Cu as a catalyst. Ever since this process is known as Ullmann reaction and becomes a basic Chemistry textbook case. Due to its varsatility to use different substituted benzenes allowing large number of products and high purity results, it is widely used in lab-style synthetic chemistry. Altogether three elementary steps involve in this reaction process; iodine dissociation from iodobenzene, migration to meet two phenyl radicals and their association to form biphenyl. Here we show that we can perform all elementary steps of Ullmann reaction over single molecules in controlled manner and can synthesize individual biphenyl molecules on the Cu(111) surface for the first time by utilising various single atom and molecule manipulation techniques with a low temperature scanning tunneling microscope (STM) at 20 K. The synthesis steps involve iodine dissociation from single iodobenzene molecules with tunneling electrons and the resulting phenyl radicals were put together by laterally moving them with STM tip. The association of two phenyl radicals to form a bi-phenyl molecule was realised by simultanuously exciting them with tunneling electrons. The threshold tunneling voltage to dissociate the iodobenzene and the energy range of phenyl oscillation on Cu(111) were determined by using I-V single molecule tunneling spectroscopy.

8:40am **NS2-TuM2 Scanning Tunneling Microscopy of Conjugated Oligomers on Si(100)***, **B. Grandidier**, J.P. Nys, D. Stievenard, C. Krzeminsky, C. Delerue,* IEMN CNRS, France*; J.M. Raimundo, P. Frere, J. Roncali,* IMMO, Universite d'Angers, France

Conjugated oligomers have attracted considerable interest as possible molecular wires. Investigation of the interaction of these molecules with the silicon (100) surface is therefore useful to gain insight into the way the oligomers could be connected to the silicon surface. The adsorption of different oligothiophenes on silicon (100) 2x1 have been studied by scanning tunneling microscopy in ultra high vacuum. The current constant images of the oligothiophenes are strongly bias dependent and allow the determination of the adsorption sites. The reaction involves the thiophene ring with a single Si atom of the Si=Si dimer. Ab initio calculations are performed to better characterize the chemical nature of the bonding.

9:00am **NS2-TuM3 Initial Growth of 3,4,9,10-perylenetetracarboxylic-dianhydride (PTCDA) on Au(111): A Scanning Tunneling Microscopy Study***, I. Chizhov, **A. Kahn**, G. Scoles,* Princeton University

The structure and morphology of 3,4,9,10-perylenetetracarboxylicdianhydride (PTCDA) films deposited on Au(111) surface in ultrahigh vacuum is studied via scanning tunneling microscopy (STM). In the first monolayer, PTCDA molecules form well-ordered domains with two distinct structural phases. The first phase is characterized by a "herring-bone" arrangement of PTCDA molecules similar to that of a bulk PTCDA molecular crystal. The second phase, which had not been reported so far, is characterized by a molecular arrangement in a square pattern that does not have a known bulk analog. This second phase is less dense than the first. Only the "herring-bone" phase is consistently observed in the second and subsequent layers. The crystallographic orientation of the PTCDA layers, with respect to the Au substrate as well as with respect to each other, is directly determined from the STM images. At coverages above 2 monolayers, the formation of PTCDA islands with good molecular order is observed. Transient effects related to STM-induced dynamic changes in the PTCDA molecular layer are also discussed.

9:20am **NS2-TuM4 Isolating, Imaging, and Electrically Characterizing Individual Organic Molecules on the Si(100) Surface with the Scanning Tunneling Microscope***, **M.C. Hersam**, J.W. Lyding,* University of Illinois, Urbana-Champaign

Molecular electronics shows great potential as an approach for fabricating nanoelectronic devices and circuits. Despite this potential, many fundamental problems remain unsolved. This paper outlines a three pronged approach that addresses key molecular electronic issues for molecules supported on STM-patterned hydrogen passivated Si(100) surfaces. First, feedback controlled lithography (FCL) has been developed as a reliable technique for making templates of individual dangling bonds on the Si(100):H surface. FCL detects individual H desorption events while patterning, thereby compensating for variations in tip structure. When the surface is then exposed to a flux of molecules, they bind individually to the prepatterned sites. With this technique, norbornadiene and copper phthalocyanine molecules have been intentionally isolated into predefined patterns. STM images reveal intramolecular detail and suggest mechanical behavior such as molecular rotation. Secondly, using STM spectroscopy, molecules' electronic properties have been revealed. Filled states tunneling conductance maps of copper phthalocyanine molecules exhibit an enhanced density of electronic states. However, in empty states, a ring of reduced local density of states surrounds each copper phthalocyanine molecule. Further multi-bias images reveal a more complex intramolecular electronic structure that helps to differentiate among the possible binding configurations of the molecule. Finally, an all-UHV scheme for isolating and, ultimately, electrically contacting STM-patterned nanostructures has been developed that utilizes a pre-defined p-n junction on a Si(100) substrate. With STM potentiometry, the junction is easily located, allowing for efficient registration of nanostructures after intermediate processing steps. In addition, by STM patterning across the depletion region, the electrical properties of selectively deposited nanostructures can be directly evaluated when the p-n junction is biased.

9:40am **NS2-TuM5 Molecular Wires and Molecular Junctions: Tunneling, Injection and Transport***, **M.A. Ratner**,* Northwestern University **INVITED**

Molecular wires, molecular interconnect structures, molecular emission devices and, indeed, much of molecular electronics requires efficient control of charge transport processes at the molecule/electrode interface. Direct measurements on individual molecular transport junctions are beginning to appear, and will be featured in this symposium. Understanding the conductance properties of molecular junctions requires a computational model that deals effectively with both the continuum (electrode) and discrete (molecular) aspects of the issue. The problem is similar to that of chemisorption, and the Hamiltonian models discussed are also similar. Because of this discrete/continuum coupling, the molecular levels are shifted and broadened. This leads to self energies that describe the effective state densities for injection and transport. The use of Landauer type expressions then leads to specific predictions for voltage dependence conductance in the coherent regime; most measures of individual junctions reported to date indeed can be characterized in this way. For actual injection and dissipative charge transport, the Landauer model is no longer appropriate. Here considerations of typical molecular behavior arise, and at least five different charge transport mechanisms can be posited. We will discuss some aspects of these mechanisms, advantages and disadvantages for long range charge transport in molecular wires, aspects of the energy dissipation problem and the energetic control of transport by design both of the molecule itself and of the interface.

10:20am **NS2-TuM7 Self-assembled Molecular Electronics: Is the Interface Conducting?***, T. Vondrak, C.J. Cramer, **X.-Y. Zhu**,* University of Minnesota

The use of a single molecule as a 'quantum dot' or 'quantum wire' in charge transport has attracted considerable attention due to its exciting potential in future electronic devices. A number of groups have studied the electron transport in single aromatic molecules using thiol self-assembled monolayers (SAMs) on gold surfaces. A critical issue in interpreting experimental current-voltage measurements and in designing self-assembled monolayer of molecular electronics is understanding the interfacial electronic structure. We present a systematic study to address the title question. We probe both occupied and unoccupied electronic states at the interface using laser two-photon photoemission spectroscopy, in conjunction with electronic structural calculations. We choose phenyl or fluorophenyl group tethered to the metal surface at various distance in self-assembled monolayers on Cu(111). We found that, for phenyl attached to Cu via the -S- linker, the molecular LUMO can be stabilized by as much as 3 eV. This large change cannot be accounted for exclusively by polarization effects. The majority of the stabilization energy must come from direct, strong electronic coupling between the substrate and the adsorbate. Ab initio calculations on model molecules confirms this conclusion. This kind of strong electronic coupling is absent when the molecule is located at a similar distance, but weakly coupled to the surface. Thus, we may view the -S-metal linker as a conducting contact in SAMs of molecular electronics. Our result also suggests the importance of sigma states for electron transport in short molecular wires.

10:40am **NS2-TuM8 Scanning Potentiometry Studies of Charge Transport in Sexithiophene-based FETs using Conducting Probe Atomic Force Microscopy (CP-AFM)***, **K. Seshadri**, T.W. Kelley, C.D. Frisbie,* University of Minnesota

Investigation of charge transport mechanisms in organic semiconductors is of immense importance to development of devices such as thin film transistors and organic-based LEDs. Of particular interest is @alpha@-sexithiophene (6T), with a hole mobility high enough for flexible, "all plastic" devices. Conducting Probe Atomic Force Microscopy (CP-AFM) has been used to measure electrical transport characteristics of 6T. The semiconductor was deposited as crystals, ranging from 1 to 6 molecules (2-14 nm) in thickness and from 1-2 µm in diameter by vacuum sublimation onto SiO2/p-Si substrates, with lithographically defined Au contacts. The semiconductor crystallite grows across the gap between two electrodes, with a capacitively coupled gate electrode, so as to achieve a field-effect transistor configuration (FET). A Au-coated conducting AFM probe is brought into contact with the electrically biased 6T crystallite, and the potential is measured as a function of position. This is a scanning potentiometry experiment, involving mapping the local potential over the surface of the organic semiconductor. Mesoscopic transport measurements, in combination with AFM imaging, are a useful strategy for elucidating charge transport across grain boundaries, charge trapping, and other structure-transport relationships in organic materials.

Organic Electronic Materials Topical Conference
Room 616/617 - Session OE+EM+AS-TuM

Interfaces and Characterization of Organic Thin Films

Moderator: Y. Gao, University of Rochester

8:20am **OE+EM+AS-TuM1 Electronic Properties of Organic Semiconductor Interfaces*, I.G. Hill,*** Princeton University*; C. Shen,* Princeton University, US*; D. Markiewicz, J. Schwartz, A. Kahn,* Princeton University **INVITED**

The alignment of molecular energy levels at the interfaces of organic semiconductor films plays a critical role in determining organic light emitting device (OLED) efficiencies. At a metal/semiconductor interface, the positions of the highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO respectively) relative to the metal Fermi level determine the barriers for charge injection into the organic. At organic/organic heterointerfaces, the relative alignment of the HOMO and LUMO levels of the two organics determines whether charges will flow freely across the interface or result in charge accumulation. It is now widely accepted that vacuum levels do not, in general, align at metal/organic interfaces,@footnote 1,2@ implying that techniques such as ultraviolet photoelectron spectroscopy (UPS) and internal photoemission must be used to determine barrier heights. Vacuum levels do align at the majority of organic/organic heterointerfaces, with a few notable exceptions.@footnote 3@ Using UPS, we have studied a variety of both metal/organic and organic/organic interfaces with the goal of understanding the origin of, and therefore ways to control, the interface dipoles which result in vacuum level discontinuities. The results of these studies will be discussed with an emphasis on our attempts to understand the roles of surface modifying procedures, such as oxygen plasma treatment of indium tin oxide (ITO), on improving device performance. @FootnoteText@ @footnote 1@H. Ishii and K. Seki, IEEE Trans. Electr. Devices 44, 1295, (1997) @footnote 2@I.G. Hill, A. Rajagopal and A. Kahn, Appl. Phys. Lett., 73, 662, (1998). @footnote 3@I.G. Hill and A. Kahn, Proceedings of SPIE, Organic Light-Emitting Materials and Devices II, 3476, 168, (1998).

9:00am **OE+EM+AS-TuM3 Photoemission Characterization of Al/Alq@sub 3@ and Al/LiF/Alq@sub 3@ Interfaces*, L. Yan,*** *Q.T. Le, Y. Gao,* University of Rochester*; M.G. Mason, C.W. Tang,* Eastman Kodak Company

We have investigated the interface formation of Al on tris-(8-hydroxyquinoline) aluminium (Alq@sub 3@) and Al on LiF/Alq@sub 3@ using X-ray and ultraviolet photoemission spectrascopy (XPS and UPS). We observed significant modifications of O1s, N1s and Al2 p core level spectra as Al was directly deposited on the Alq@sub 3@ surface. The Alq@sub 3@ features in the UPS spectra were also quickly destroyed. In contrast, a dramatically different behavior was observed for Al on the LiF/Alq@sub 3@ interface. With o nly 5Å of LiF deposited on the Alq@sub 3@ surface as a buffer layer, the reaction between Al and Alq@sub 3@ is significantly suppressed. A well-defined gap state is formed. The Alq@sub 3@ features in UPS shift to higher binding energies but remain easily recognizable. Both the core level spectra and the gap state suggest that the Alq@sub 3@ anion is formed in the presence of Al and LiF.

9:20am **OE+EM+AS-TuM4 Charge Injection vs. Chemical State of Electrode Surfaces in Metal/Alq@sub 3@/Metal Structures*, C. Shen,*** Princeton University, US*; I.G. Hill, A. Kahn,* Princeton University

The effect of the deposition sequence on the electrical behavior of metal-organic interfaces is an important issue in the context of multiple layer organic light emitting devices (OLED). Metals deposited on organics generally lead to more extensive interface chemistry, and have been reported to produce different electrical behavior, than organics deposited on metals. To address this issue, we investigate the interface chemistry, electronic structure and electrical transport in nominally symmetric Mg:Ag/8-hydroxyquinoline aluminum(Alq@sub 3@)/Mg:Ag structures fabricated and tested in ultra-high vacuum and under controlled atmosphere. We perform detailed X-ray photoemission spectroscopy measurements which confirm that the metal-organic chemical reaction and interdiffusion are different at the Mg-on-Alq@sub 3@ interface than at the of Alq@sub 3@-on-Mg interface. We also show, however, that the chemical state of the bottom electrode surface plays a major role in the device electrical behavior. The Mg:Ag/Alq@sub 3@/Mg:Ag structure built in ultra-high vacuum leads to symmetric top and bottom electron injection, whereas controlled oxidation of the bottom metal surface leads to a two-order-of-magnitude lower bottom contact injection. These results fully explain earlier results obtained for devices made under "standard" conditions, i.e. in moderate 10@super -5@ Torr vacuum. A similar study of the Al/Alq@sub 3@/Al structure is under way and will be reported as well at the conference.

9:40am **OE+EM+AS-TuM5 Investigation of the Electronic Structure of Organic Schottky Contacts with Photoemission Spectroscopy: Discrimination Between Interface Dipole, HOMO Offset, Band Bending and Charging Related Spectral Shifts*, R. Schlaf,*** *G.P. Kushto, L.A. Crisafully, C.D. Merritt, Z.H. Kafafi,* US Naval Research Laboratory

We have determined the electronic structure of several organic Schottky contacts formed between the organic luminescent semiconductor tris (8-hydroxyquinolinato) gallium (Gaq@sub 3@) and the metals Al, Mg, Ag, Au, and Pt. The investigated interfaces were prepared by vapor deposition of Gaq@sub 3@ on in-situ deposited metal films or thin sputtered high purity metal foils in a multi step growth procedure. Before growth and after each Gaq @sub 3@ deposition step the samples were characterized in situ using a combination of x-ray and ultraviolet photoemission spectroscopies (XPS, UPS). UPS was used to measure the highest occupied molecular orbital (HOMO) positions and interface dipoles, while XPS was used to determine the band bending (bulk charge redistribution) at the interface. In addition, simultaneous measurements of the high binding energy cutoff of the XP- and UP-spectra allowed the determination of the onset of charging phenomena observed at around 100Å Gaq@sub 3@ film thickness. Our results demonstrate that both, charging and band bending effects, may result in strong shifts of the PES spectra which need to be carefully evaluated in order to accurately determine the orbital line-up and the dipole at the interface. Our experiments suggest that the investigated organic Schottky contacts have large interface dipoles due to the chemisorption of the first organic layer in contact with the metal surface. All investigated interfaces also exhibit strong band bending in the organic layer, which strongly depends on the work function difference between Gaq@sub 3@ and the particular metal in contact.

10:00am **OE+EM+AS-TuM6 Examination of Band Bending at Organic Semiconductor / Metal Interfaces Studied by Kelvin Probe Method*, H. Ishii,*** *N. Hayashi, E. Ito, K. Seki,* Nagoya University, Japan

How the energy levels of an organic semiconductor and a metal electrode align at the interface between them is a critical and basic issue for understanding organic electronic devices. So far, Mott-Schottky (MS) model has been applied for the estimation of the electronic structure at organic/metal interfaces. In the model, vacuum level alignment is assumed right at the interface, while the Fermi level alignment is achieved through band bending in space charge layer. In order to examine the validity of this model, the film-thickness dependence of the location of the vacuum level of TPD (N,N'-bis(3-methylpheyl)-N,N'-diphenyl-[1,1'-biphenyl]-4,4'-diamine) on various metals(Au, Cu, Ag, Mg and Ca) were measured by Kelvin probe method in ultrahigh vacuum (UHV). At all the interfaces, an abrupt shift of the vacuum level was observed within 1 nm thickness, while further deposition of TPD up to 100 nm led to no change of the location of the vacuum level. These results indicate that the possible space charge layer is much thicker than 100 nm in UHV. The observed relation between the vacuum level shift and the work function of the metals suggests that (1) the Fermi level of TPD is located around the midgap in UHV condition and that (2) the Fermi level alignment is achieved only at TPD/Cu,Ag,Mg interfaces, not by band bending but by dipole layer formation right at the interface. These findings clearly demonstrate the invalidity of MS model for organic / metal interfaces in UHV. The results for the interface between Alq@sub 3@ (tris(8-hydroxyquinolino)aluminum) and metal will be also presented.

10:20am **OE+EM+AS-TuM7 Schottky Energy Barriers and Charge Injection at Metal/Organic Interfaces*, I.H. Campbell,*** Los Alamos National Laboratory*; B.K. Crone,* Lucent Technologies*; R.L. Martin, D.L. Smith,* Los Alamos National Laboratory*; C.J. Neef, J.P. Ferraris,* University of Texas, Dallas **INVITED**

We present independent measurements of metal/organic Schottky energy barriers and their charge injection characteristics in metal/organic/metal structures. The Schottky energy barriers were measured using internal photoemission and built-in potential techniques. The Schottky energy barriers to a poly (p-phenylene vinylene) based polymer (MEH-PPV) and to Alq were measured for a variety of metals with work functions ranging from 2.7 eV (Sm) to 5.6 eV (Pt). For MEH-PPV we find good agreement with the ideal Schottky model. In contrast, for Alq we find that the ideal Schottky picture is not applicable and that electron injecting contacts are pinned about 0.6 eV below the electron conducting states. The charge injection characteristics of these contacts were investigated by measuring the current-voltage characteristics of single carrier structures. The dependence of the current-voltage characteristics on the Schottky energy barrier is quantitatively described by a device model which includes charge injection, transport and space charge effects in the structure. For Schottky barriers less than about 0.3 eV the current in the structure is space charge limited and the contact is ohmic. Finally, we present results using organic self-assembled monolayers to manipulate the metal/organic Schottky energy barrier and to control charge injection into the organic material. The monolayers are used to insert a thin (1 nm) dipole layer between the metal contact and the organic material. Depending upon the orientation of the dipole layer the Schottky energy barrier may be increased or decreased and the corresponding charge injection properties degraded or enhanced.

11:00am **OE+EM+AS-TuM9 Interfacial Electronic Structures between p-Sexiphenyl and Metals Studied by Electron Spectroscopies*, E. Ito,*** *H. Oji, H. Ishii, Y. Ouchi, K. Seki,* Nagoya University, Japan

Recently, organic electroluminecent (EL) devices have attracted much attention in relation to application to flat panel display. In order to understand the charge injection mechanism in such devices, the energy level alignment at the interfaces between organic films and metal electrodes is of crucial importance. In this study, we investigated electronic structures at the interfaces between p-sexiphenyl (6P) and a metal (Au or Mg) by ultraviolet photoelectron spectroscopy (UPS), metastable atom electron spectroscopy (MAES), and X-ray photoelectron spectroscopy (XPS). MAES is an extremely surface sensitive method because the excitation source is metastable atoms which can not penetrate into a sample. The abrupt shift of the vacuum level by 6P deposition on the evaporated metal film (Au or Mg) was observed in the UPS spectra. MAES spectrum of 6P on Au with the thickness of 0.3nm is almost similar with that of 20nm thick 6P film. This suggests that the flat-lying 6P molecules uniformly covered Au substrate. We also measured the spectra of Au on 6P/Au. Even when Au was evaporated with the thickness of 50nm, the spectral feature of 6P dominates in the MAES spectra, suggesting that Au does not cover completely with the 6P film, while the core level peak of Au gradually increased in XPS spectra with deposition of Au. Similar trend was also observed for Mg deposited on 6P/Mg. These results indicate the diffusion of Au into 6P film, leading to formation of the intermixing region. In the system of Au on 6P film, we observed downward shift of the energy levels with irradiation of UV-light (the excitati on source of UPS), probably due to the photovoltaic effect. These results show the the formation of the different interface between the 6P/metal and the metal/6P.

11:20am **OE+EM+AS-TuM10 A Photoemission Investigation of Interfaces of poly(2, 5-diheptyl-1,4-phenylene-alt-2,5-thienylene) with an oligomer (p-sexiphenyl) and a Metal - Calcium*, A. Rajagopal,*** Univ. Notre-Dame, Belgium*; N Koch,* Tech. Univ. Graz, Austria*; J Ghijsen,* Univ. Notre-Dame, Belgium*; K. Kaeriyama,* Kyoto Inst. of Tech., Japan*; R.L Johnson,* Univ. Hamburg, Germany*; G. Leising,* Tech. Univ. Graz, Austria*; J.J. Pireaux,* Univ. Notre-Dame, Belgium

Poly(2, 5-diheptyl-1,4-phenylene-alt-2,5-thienylene) (PDHPT) is a blue light emitting conjugated polymer with a band gap of ca. 3 eV, and is a promising candidate as an active material in organic light emitting diodes. The interface of this polymer with a) a blue light emitting oligomer (sexiphenyl- 6P), and with b) a low work function cathode material, calcium (Ca) have been investigated using both ultraviolet and x-ray photoelectron spectroscopy (UPS and XPS). Both 6P and PDHPT have a band gap of ca. 3 eV, as well as similar ionization potentials, and this makes the interface an interesting one. A systematic study of the in-situ growth of 6P on PDHPT allows the estimation of the relative positions of the HOMOs and the vacuum levels. We find that the HOMO of PDHPT is below that of 6P, and there is a vacuum level offset of 0.3 eV suggesting charge transfer from 6P to PDHPT. In the case of metal-PDHPT interface, Ca was deposited in extremely small steps in-situ, and both XPS and UPS data were recorded after each subsequent deposition. Contrary to what can be predicted based on calculations and experiments on similar systems, namely phenylenes and thiopehenes, we propose that Ca forms covalent bonds with the polymer. The consequences of these experimental findings will be discussed within the context of LEDs.

11:40am **OE+EM+AS-TuM11 A Photoelectron Study of Chemically Treated Indium Tin Oxide Surface and Its Reactivity with Phenyl-Diamine*, Q.T. Le,*** *F. Nuesch, E.W. Forsythe, L.J. Rothberg, Y. Gao,* University of Rochester

We report on the effect of various treatments by base and acid solutions on the work function of indium tin oxide (ITO). Ultraviolet and x-ray photoelectron spectroscopy (UPS and XPS) were used to measured the work function and chemical composition, respe ctively, of the processed ITO surface. The results indicate that the magnitude of the work function shift is highly dependent on the nature of the solution. In contrast, for the same solution, the concentration of the solution appears to have little effe c t on the work function shift. In addition, the interface formation between processed ITO and N,N'-bis-(1-naphthyl)-N,N'-diphenyl-1,1'-biphenyl-4,4'-diamine (NPB) using XPS and UPS is presented. The reactivity of the treated ITO surfaces versus NPB is co mp ared with the case of plasma-treated sample. The low current onset obtained from the single-layer devices based on acid-treated ITO can be attributed to the low energy barrier for hole injection at the ITO/hole-transporting material interface. This work was supported in part by DARPA DAAL 0196K0086, NSF Grant DMR-9612370, and the Swiss National Science Foundation.

Plasma Science and Technology Division
Room 609 - Session PS-TuM

Plasma-Surface Interactions I

Moderator: R.L. Jarecki, Sandia National Laboratories

8:20am **PS-TuM1 Probing Surface Layers during Inductively Coupled Plasma Etching using Laser-Thermal Desorption and Other Optical Techniques*, I.P. Herman,*** *J.Y. Choe, N.C.M. Fuller,* Columbia University*; V.M. Donnelly, M.V. Malyshev, K.H.A. Bogart,* Bell Laboratories, Lucent Technologies **INVITED**

The etching of Si, Ge, and InP by an inductively coupled plasma (ICP) of chlorine is investigated by analyzing both the composition of the surface and the plasma during etching. The surface is probed by using laser-induced thermal desorption with an XeCl laser (308 nm) to desorb the steady-state adlayer and optical methods to detect these desorbed species. The development of a new method to detect optically these laser desorbed (LD) species is detailed, that of examining transient changes in the plasma-induced emission (PIE). This LD-PIE method is seen to be more universal than the previously reported detection by laser-induced fluorescence (LD-LIF), but is seen to require more calibration due to varying electron density and temperature with varying plasma conditions. This is detailed for Si etching, for which LD-PIE and LD-LIF results are compared. The calibration methods are seen to be valid when the surface is analyzed as the rf power supplied to the reactor is varied. A more complete picture of the etching process requires detailed characterization of the plasma through measurements of the constituents of the plasma. Neutral Cl@sub 2@ and Cl densities are determined by optical emission actinometry; Cl@sub 2@@super +@ and Cl@super +@ densities are determined by LIF and Langmuir probe measurements; and electron densities - needed for LD-PIE calibration - are measured by microwave interferometry. An improved understanding of the etching mechanism is obtained by combining the results of each of these measurements. This work was supported at Columbia by NSF Grant No. DMR-98-15846.

9:00am **PS-TuM3 Microscopic Uniformity in Oxide Etch during Overetch Time in Polysilicon Gate Etching*, K. Ono,*** Kyoto University, Japan*; T. Mutumi,* Mitsubishi Electric Corporation, Japan

Plasma-surface interactions during polysilicon gate etching have been studied in ECR Cl@sub 2@ and Cl@sub 2@/O@sub 2@ plasmas, with emphasis on a better understanding of competitive mechanisms for microscopic uniformity i n etching of underlying SiO@sub 2@ that occur during overetch time. Experim ents were performed as a function of pressure, O@sub 2@ percentage, and rf b ias power, using samples for etching masked with a photoresist pattern of li nes and spaces (0.35-5 µm). The results of SiO@sub 2@ etching exhibit ed aspect-ratio dependent etch rates similar to those of poly-Si. In pure C l@sub 2@ plasmas, an RIE lag was observed at relatively low pressures (20%) was muc h larger for SiO@sub 2@ than for poly-Si. The inverse RIE lag also occurred at high pressures in pure Cl@sub 2@ plasmas, probably owing to background o xygen. Moreover, microscopically nonuniform thinning and breaking of thin g ate oxides was found to occur during overetch time; the thinning and breakin g occurred preferentially in large open fields in pure Cl@sub 2@ plasmas, wh ile in dense areas at high level O@sub 2@ addition in Cl@sub 2@/O@sub 2@ pla smas. A comparison of the experiments with the predictions of rate model an alysis indicated that the microscopic uniformity of SiO@sub 2@ etch rate pre sently observed in chlorine-containing plasmas is interpreted in terms of tw o competing processes caused by incoming ions and neutrals from the plasma i nto microstructures: carbon-enhanced oxide etching and removal of carbonaceo us materials by oxygen. The carbonaceous materials of interest are attribut able primarily to hydrocarbon fragments from sputtered photoresist, and the background and/or added oxygen is assumed to scavenge such hydrocarbon fragm ents adsorbed on SiO@sub 2@ surfaces before they enhance the oxide etch rate.

9:20am **PS-TuM4 Vacuum Beam Studies of Photoresist Etching Kinetics***, **F. Greer**, J.W. Coburn, D.B. Graves,* University of California, Berkeley

One factor limiting the development of reliable models of high density, low pressure oxide etch plasmas is the relatively poor understanding of the plasma-photoresist surface interactions. In particular, the relatively high rates of photoresist (PR) loss experienced in high density fluorocarbon plasmas is a significant problem. It has long been accepted that fluorine plays a key role in controlling the oxide to PR etch rate selectivity. The addition of hydrogen has been shown to improve this selectivity by scavenging fluorine from the tool. To develop reliable models of these etch tools, it is necessary to understand how this process occurs and to predict PR etch rates as a function of the neutral to ion flux ratio at the surface as well as the ion energy dependence. The neutral and ion compositions in practical etch systems are difficult to measure and control accurately; however, vacuum beam systems can probe the plasma-surface interactions of various samples by employing independent beams of both neutral and ionic species. The complicated chemistry of fluorocarbon plasmas is modeled with argon ions and independent neutral fluxes of hydrogen and fluorine atoms intersecting at the surface of a photoresist sample. We will present experimental evidence that the etch yield of photoresist (carbon atoms removed per incident argon ion) under these conditions is quite high compared to that of silicon and silicon dioxide. The presence of a simultaneous flux of hydrogen on the photoresist surface does not affect the etch yield measured despite the fact that HF does form during the etching process. In addition, the relative reactivity of hydrogen and fluorine atoms for abstraction of one another on the photoresist surface has been measured with modulated beam mass spectrometry with and without ion bombardment. These results are incorporated into a phenomenological model of the photoresist etching process.

9:40am **PS-TuM5 The Relationship of Etch Reaction and Reactive Species Flux in C@sub 4@F@sub 8@/Ar/O@sub 2@ Plasma for SiO@sub 2@ Selective Etching Over Si@sub 3@N@sub 4@***, **M. Matsui**, T. Tatsumi, M. Sekine,* Association of Super-Advanced Electronics Technologies (ASET), Japan

The relationship between reactive species flux and their inducing surface reaction layer was studied in a SiO@sub 2@/Si@sub 3@N@sub 4@ highly selective etch process. C@sub 4@F@sub 8@/Ar/O@sub 2@ plasma in a dual-frequency (27/0.8 MHz) parallel plate etch system was employed to etch the specimens that were quantatively analyzed by using X-ray photoelectron spectroscopy (XPS). CF@sub x@ radical flux was controlled by adjusting the C@SUB 4@F@SUB 8@ flow rate ratio. The influence of the O@SUB 2@ partial pressure was also investigated. Ion flux (6 x 10@super 16@ cm@super -2@s@super -1@) and the Vpp of bias rf (1450 V) were kept constant. We have found that the etch rates strongly depend on the fluorocarbon film thicknesses. Under higher Si@sub 3@N@sub 4@ etch rate conditions with low CF@sub 2@ flux or high O@sub 2@ partial pressure, the fluorocarbon film on the Si@sub 3@N@sub 4@ surfaces was thinner than film in a high-selectivity condition (5-6 nm). The oxidation of the Si@sub 3@N@sub 4@ surface was also observed. On the other hand, the fluorocarbon film thicknesses on the SiO@sub 2@ surface were less than 1 nm where the etch reaction proceeds on the SiO@sub 2@ surface. The fluorocarbon films on SiO@sub 2@ were thinner than films on Si@sub 3@N@sub 4@ at the same CF@sub x@-radical-flux. This difference of the film thickness is considered to be due to the outflux of oxygen from SiO@sub 2@, that can remove CF species from the SiO@sub 2@ surface. The fluorocarbon films on the SiO@sub 2@ are so thin that the ion energy is not reduced when passing through the films, while those on the Si@sub 3@N@sub 4@ are almost as thick as the ion range of 1450 V. In conclusion, highly selective etch is achieved in the condition where the minimum partial pressure of O@sub 2@ and proper amount of CF@sub x@ radical flux in order to control the fluorocarbon film thicknesses on Si@sub 3@N@sub 4@ and SiO@sub 2@. @FootnoteText@ This work was supported by NEDO.

10:20am **PS-TuM7 Anisotropic Etching of Polymer Films by High Energy (~ 100s of eV) Oxygen Atom Neutral Beams***, S. Panda, **D.J. Economou**,* University of Houston*; L. Chen,* Chen Laboratories

As microelectronic device dimensions continue to shrink, charging damage is becoming a major issue. Charging damage can result in anomalous etch profiles (notching) and reduced etch rate in high aspect ratio features (aspect ratio dependent etching), in addition to thin oxide breakdown. A way to minimize or eliminate charging damage is to use a neutral beam instead of reactive ion etching. High flux, controlled energy, and high directionality are critical requirements of such neutral beam. We have developed a neutral beam reactor that generates a collimated, high energy (30-300 eV), high flux (equivalent of several mA/cm2) neutral beam. An inductively coupled source is used to generate a high density plasma. Positive ions are extracted through a grid with high aspect ratio holes, which also serves to neutralize the ions. The neutral beam reactor was tested by etching a polymer film using an O-atom beam extracted from an oxygen plasma. High rate (~ 1 micron/min), microloading-free, high aspect ratio etching, with straight sidewalls was demonstrated. The plasma source and the region downstream of the gird were characterized by optical emission actinometry and Langmuir probe measurements to shed light on the effect of source operating parameters (pressure, power, extraction voltage) on species densities and fluxes, and the degree of ion neutralization.

10:40am **PS-TuM8 X-ray Photoelectron Analysis of Sidewall Passivation Films formed during Sub 0.1 µm Silicon Gate Etch Processes***, **L. Desvoivres**,* France Telecom-CNET, France*; L. Vallier,* France Telecom-CNET and CNRS*; O. Joubert,* France Telecom-CNET and CNRS, France

As integrated circuits dimensions are rapidly scaling down to 0.1 µm regime and below, the critical dimension (CD) control of the etched features becomes more and more challenging. The critical dimension budget (10% of the nominal dimension) is usually shared between lithography and etching. Each individual step should be carefully optimized. For silicon gate applications, CD variations across the wafer are usually attributed to etch non-uniformities. However, the passivation layer which forms on the silicon sidewalls has also a direct impact on CD control since the passivation layer thickness is aspect ratio dependent. In the future, a careful control of the nature and thickness of this layer will become critical. In this work, we have investigated the impact of the chemistry (hydrogen bromine, chlorine with different oxygen dilutions) and of the plasma conditions on the formation of the sidewall passivation film. This study has been performed in a high density plasma Helicon source, operated at low pressure. The sidewall film has been analyzed using x-ray photoelectron spectroscopy. The sidewall passivation film formed in 125 nm L/S features is a 2 nm thick SiO@sub 2@ like film composed of oxygen, halogen and silicon. This film is mainly formed during the main etch step of the process thanks to etch products deposition on the sidewalls of the features. It gets oxidized at the very beginning of the overetch step thereby allowing halogen to be desorbed and the oxygen concentration to be increased. The impact of the plasma operating conditions and chemistry on the nature and thickness of the sidewall film will be presented. @FootnoteText@ @footnote 1@ This work has been carried out within the GRESSI Consortium between CEA-LETI and France Telecom-CNET

11:00am **PS-TuM9 Kinetic Roughening of GaAs (001) During Plasma Chemical Etching***, **S.W. Robey**,* National Institute of Standards and Technology

Kinetic roughening of the GaAs(001) surface during plasma etching by H and CH@sub 3@ radicals was investigated using atomic force microscopy in combination with RHEED and Auger spectroscopy. The evolution of the surface morphology was tracked as a function of etching time, temperature, and plasma composition. Large changes in the form of the surface roughness were observed and reflect variations in the surface dynamics which induce correlations from point-to-point on the surface. These changes involved not only the length scale of surface features, but also distinctive variations in the anisotropy between [110] and [-110], particularly as a function of surface temperature. Surface height data were analyzed to extract height correlation functions, which provided dynamic and roughness scaling exponents for comparison with theory. Measured height-difference correlation functions displayed two distinct roughness scaling regimes with a crossover that increased from ~ 30 nm to ~ 150 nm with increasing surface temperature between 500 K and 700 K. At short length scales, a roughness coefficient of ~ 0.7 was typically observed, while a logarithmic dependence was generally observed at larger length scales. Calculated height-correlation functions based on continuum models that include competition between short length-scale surface diffusion and long-range desorption dynamics reproduce this crossover behavior and offer the potential for extracting information on changing surface dynamics as a function of etch conditions.

11:20am **PS-TuM10 Measurements and Modeling of the Absolute Sputtering Yield of Nitrided and Non-nitrided Diffusion/Barrier Film Materials with Incident N+ and Ar+**, ***R. Ranjan**, M.H. Hendricks, J.P. Allain, D.N. Ruzic,* University of Illinois, Urbana-Champaign

The angular distribution of sputtered material and the absolute sputtering yield of metal targets by argon ions at energies less than 1000 eV has been measured in previous work for a number of materials.@footnote 1@ The application of TiN and TaN films for both diffusion barrier and enhanced metallization properties has grown in the advent of copper metallization. The conformal nature of such diffusion barriers has been addressed with the advancement of IPVD magnetron sputtering systems. In order to understand the physical processes on magnetron targets used in such systems, an experiment in the Ion-surface InterAction Experiment (IIAX) facility has been designed to measure the absolute sputtering yield of nitrided and non-nitrided barrier/seed layer material targets with incident N and Ar ions. A Coultron ion source is used to create and accelerate gaseous ions onto a 100 mm@super 2@ metal target. The bombarding ions are mass-selected through an E X B filter and decelerated near the target. The target can be rotated in order to provide variation in the angle of incidence. A plasma cup is used to remove the first few monolayers and thus provide a "clean" surface. This method also provides for "nitriding" the layer on the target surface. A newly designed dual quartz crystal oscillator unit is rotated in front of the target to collect the sputtered flux measuring the absolute sputtering yield. Modeling is performed by VFTRIM3D, an enhanced version of TRIM, a Monte Carlo code which includes fractal geometry and a non-binary collision model.@footnote 2@ @FootnoteText@ @footnote 1@ P.C. Smith, D.N.Ruzic, submitted, J. Vac. Sci. Technol.A @footnote 2@ D.N.Ruzic, Nuclear Instrum. and Methods in Phys. Res. B47 (1990) pp.118-125

Surface Science Division
Room 606 - Session SS1+EM-TuM
Nitrides and Compound Semiconductors

Moderator: A.C. Kummel, University of California, San Diego

8:20am **SS1+EM-TuM1 Reconstructions and Growth Kinetics of GaN Surfaces with and without Adlayers**, ***R.M. Feenstra,*** Carnegie Mellon University **INVITED**

Reconstructions of the gallium nitride (0001) Ga-face and N-face surfaces have been studied using scanning tunneling microscopy, with growth performed by molecular beam epitaxy. Distinct families of reconstruction are observed on each face, with most of the structures involving the presence of one of more adlayers of gallium bonded to underlying nitrogen atoms. For the N-face, this Ga-adlayer is in a 1x1 arrangement and further reconstructions are formed by additional Ga adatoms weakly bonded on the Ga-adlayer. For the Ga-face, the Ga-adlayer is incommensurate with the GaN lattice. For both the Ga- and N-face, growth under Ga-rich conditions yields smooth surfaces whereas growth under N-rich conditions produces rough surfaces. The latter case is indicative of limited surface diffusion rates. However, in the presence of surfactant layers such as Mg or As, smooth growth is also obtained in the N-rich regime. For sufficiently high surface coverage of Mg, a remarkable transition is observed in which Ga-polar material converts to N-polarity, with the inversion domain boundary extending along the c-plane. For growth of InGaN alloys, the role of surface metal layers (mainly indium) is also found to play an important role in the growth kinetics and incorporation efficiency. @FootnoteText@ Work supported by Office of Naval Research and National Science Foundation, and performed in collaboration with V. Ramachandran, H. Chen, A. Smith, D. Greve, J. Northrup, J. Neugebauer, W. Sarney, and L. Salamanca-Riba.

9:00am **SS1+EM-TuM3 Increase of Electrical Conductivity in p-GaN by Immersion in H@sub2@O@sub2@ Solution***, ***B. Liu,** M.H. Ahonen, P.H. Holloway,* University of Florida

Immersion in a peroxide solution was found to increase electrical conductivity in p-GaN films. Auger electron spectroscopy (AES), current-voltage and Hall measurements were used for characterization. All samples in this study were grown on the c-plane of sapphire substrates by metallorganic vapor phase epitaxy (MOVPE) with a carrier concentration of 1.1x10@super 17@ cm@super -3@. The samples were first cleaned in boiling aqua regia (3HCl+3HNO@sub 3@) for 10min, rinsed in DI water, and blown dry with N@sub 2@. Metal contacts (10nmNi/100nmTi/100nmAu) were deposited with an electron beam evaporator (~10@super -6@ Torr). After metal deposition, samples were immersed in a H@sub 2@O@sub 2@ solution (1H@sub 2@O@sub 2@ : 5H@sub 2@O or 1H@sub 2@O@sub 2@ : 1H@sub 2@O, in volume) for different time (30sec to 300sec). This was followed by DI water rinse and N@sub 2@ blowing dry. Surface composition analysis using AES showed differences in N concentration versus treatments with the highest increase of N (5.67at%) found after immersion in 1H@sub 2@O@sub 2@ : 1H@sub 2@O for 300sec. Corresponding to this increase in N, improved electrical conductivity was confirmed by current-voltage data. The highest (a factor of two) increase of conductivity was measured for the sample with the highest increase of N concentration. No increase of carrier concentration was found in these samples with Hall measurement. The increase of N atoms at the sample surface and improvement of electrical conductivity will be discussed based on the chemical reaction of H@sub 2@O@sub 2@ with GaN and the effects of N vacancies in p-GaN. * This work is supported by EPRI and DARPA under agreement W08069-07.

9:20am **SS1+EM-TuM4 Structure of GaN(0001)-1*1: Holography Study of Mg Adsorption on GaN(0001) Surface**, ***G.J. Lapeyre**, S.H. Xu, H. Cruguel, Y. Yang,* Montana State University; *J.F. Schetzina,* North Carolina State University

The adsorption site and surface atomic structure of Mg on GaN(0001)-1*1 surface has been studied by photoelectron holographic imaging technique. The results clearly show that Mg adsorbs on T4 site and there is one monolayer Ga adatoms on the surface. They are on H3 sites.

9:40am **SS1+EM-TuM5 Angle Resolved Photoemission Studies of the Surface Electronic Structure of GaN(0001)**, ***K.E. Smith**, Y.C. Chao, P. Ryan, J. Downes, C.B. Stagarescu, R. Singh, T.D. Moustakas,* Boston University; *D. Hanser, R.F. Davis,* North Carolina State University

The physical properties of GaN are under intense study due to its use in optoelectronic and high temperature semiconductor devices. However, the surface electronic structure of GaN remains poorly understood. Numerous reconstructions of GaN are observed, but very little is known about the detailed electronic structure of clean, ordered GaN surfaces. We report the results of an extensive synchrotron radiation excited angle-resolved photoemission study of n-type and p-type wurtzite GaN(0001)1x1 surfaces. GaN thin films were grown both by MOCVD on SiC, and by MBE on Al@sub 2@O@sub 2@. Surfaces were cleaned by repeated cycles of N@super 2+@ ion bombardment followed by annealing in UHV. We have observed a number of different surface states on these materials. For n-type MBE samples we find a non-dispersive surface state just below the valence band maximum that is highly sensitive to surface contamination and disorder. This state shows no dispersion perpendicular to the surface and exists across the surface Brillouin zone in a region devoid of bulk states. Polarization measurements reveal that this feature originates from a state with sp@sub z@ character. Destruction of this state only partially removes the observed band bending. For n-type MOCVD samples, cleaned in an identical fashion, we find at least two surface states. One is similar to that seen on the MBE material, while the second is a highly dispersive back bonding state, extending to the bottom of the valence band at points in the surface Brillouin zone. Removal of these states does not alter the observed band bending. For p-type MBE samples, we also find a surface state in the fundamental band gap, above the valence band maximum. Such states are not observed for the n-type material. We will discuss the surface electronic structure of GaN in the context of these measurements. @FootnoteText@ Work supported in part by NSF grant DMR 95-04948. Experiments were performed at the NSLS, which is supported by US DOE.

10:00am **SS1+EM-TuM6 The Reaction of Oxygen with GaN(0001)**, ***B.D. Thoms,*** Georgia State University, US; *V.J. Bellitto, Y. Yang,* Georgia State University; *D.D. Koleske, A.E. Wickenden, R.L. Henry,* Naval Research Laboratory

In addition to optoelectronic applications, Group III Nitrides also exhibit properties appropriate for their use in high power and high temperature transistors. Oxidation of the surface influences several aspects of device fabrication including surface passivation and the production of metal contacts. We have characterized the reaction of oxygen with MOCVD-grown GaN(0001) using low energy electron diffraction (LEED), Auger electron spectroscopy (AES), energy loss spectroscopy (ELS), high resolution electron energy loss spectroscopy (HREELS), and temperature programmed desorption (TPD). AES of GaN(0001) following exposure to O2 at room temperature results in an increased O(KLL) Auger intensity which saturates after approximately 200 L. AES following heating shows that oxygen is present to temperatures of 900 C. No surface reconstruction is observed by LEED, but rather a reduction in contrast between diffraction spots and background with increasing oxygen exposure. The reaction with oxygen produces a reduction in the ELS intensity at loss energies of 3.5 and 6 eV. A similar reduction is observed after exposure to atomic hydrogen, consistent with the reaction of both oxygen and hydrogen with surface dangling bonds. Oxygen exposure also produces an increase in ELS intensity at 10 eV. In HREEL spectra acquired following oxygen exposures up to 200 L, no adsorbate vibrational features are resolved from Fuchs-Kliewer phonon losses at integer multiples of 700 cm-1. These data are consistent with the chemisorption of oxygen on Ga sites.

10:20am **SS1+EM-TuM7 Deep Level Electronic States of Clean GaN (0001)(1x1) Surfaces Prepared by In Decapping**, ***A.P. Young***, *L. Brillson,* Ohio State University; *C. Tu,* University of California, San Diego

The tremendous interest in the properties of GaN surfaces and interfaces has created a need for new techniques for preparing clean, ordered surfaces under ultrahigh vacuum (UHV) conditions. Furthermore, the electronic properties associated with different interface preparations are not well understood at present. In contrast to surfaces prepared by N+ bombardment or Ga overcoat annealing cycles at 900C, clean and ordered GaN (0001) (1x1) surfaces can be produced directly from MBE-grown surfaces after removal of an In cap layer at 650C. These surfaces are comparable to those clean, ordered surfaces reported elsewhere. We have used electron-excited nanometer luminescence spectroscopy (EENLS) to measure these states in the band gap of MBE-GaN deposited on a GaN/sapphire composite substrate. The GaN was cleaned in UHV via thermal desorption of a thin (~50 ML) metallic In layer deposited prior to removal of the specimen from the growth chamber. This relatively low temperature desorption presents a benign method of transporting and processing GaN for device applications. Auger Electron Spectroscopy (AES) results show that if the In can uniformly cover the surface, it can prevent contamination during atmospheric exposure without reacting or diffusing into the GaN layer. The as-prepared surface morphology, measured via ex situ atomic force microscopy (AFM), indicated significant islanding of the In on the surface with approximate lateral size of 250 nm and height of 30 nm. Furthermore, a Ga signal, probably in the form of an oxide, was observed via AES indicating that some of the surface was not covered by In. The In was selectively desorbed from the GaN without reacting to produce InGaN. 8 ML of Ga were then deposited and the surface flashed once to 690C to reduce residual O and C contamination yielding a sharp (1x1) low energy electron diffraction (LEED) pattern. EENLS at a probe energy of 350 V (probe depth » 3 nm) indicated substantial "yellow" (YL) emission within the bandgap centered at 2.22 eV (FWHM = 0.4 eV) with only minimal near band edge (NBE) emission. YL emission remains constant while NBE increases with depth of excitation, indicating only states intrinsic to the GaN bulk. Subsequent AFM reveals Ga droplets residual to the flash annealing. Thus, In decapping introduces no new states at the clean, ordered GaN surface.

10:40am **SS1+EM-TuM8 Characterization of MOCVD ZnO Buffer Layers for CIS Solar Cells**, ***L.C. Olsen,*** Washington State University; *G.J. Exarhos,* Pacific Northwest National Laboratory; *F.W. Addis, L. Huang,* Washington State University

This paper concerns studies carried out to characterize MOCVD ZnO films grown for buffer layers in CIGS solar cells which have exhibited efficiencies between 12 and 14%. Further understanding of properties of these devices are required in order to increase efficiencies above 18% as demonstrated by CIGS cells with CdS buffer layers. Work is focusing on buffer layers grown with a two step process involving nucleation of ZnO at 250 C and subsequent growth at 100 C to achieve a total film thickness on the order of 800 A. The purpose of this work is to characterize the physical and electro-optical properties of MOCVD ZnO layers, and relate the results to device processing. All ZnO films examined were grown onto copper-indium-diselenide (CIS) substrates. XPS examination of films for which the growth was terminated at various stages of the two-step process show that good coverage of CIS is achieved after 100 A of growth, although some outdiffusion of indium does occur. XPS analyses of 800 A films indicate the MOCVD ZnO films have no major impurities and that films are slightly oxygen deficient. Ellipsometry studies indicate that results for the index of refraction and extinction coefficient vs photon wavelength are well understood if one assumes that there are no secondary phases between the ZnO buffer layer and CIS, and that the ZnO band structure is characterized by three transitions, one at 3.2 to 3.4 eV, one at 3.8 to 4.0 eV, and one at 4.8 to 5.2 eV. The transitions are fairly consistent with theoretical results for the ZnO band structure. Raman spectroscopic studies of the ZnO buffer layers are also being carried out. Finally, results for ZnO buffer layers grown with the two-step process will be compared to characteristics of films grown with different procedures and which yield poor performing cells.

11:00am **SS1+EM-TuM9 Photoelectron Diffraction of GaSe Bilayer Grown on Si(111)**, ***S. Meng,*** *B.R. Schroeder, A. Bostwick,* University of Washington; *E. Rotenberg,* Lawrence Berkeley National Laboratory; *F.S. Ohuchi, M.A. Olmstead,* University of Washington

Initial nucleation of GaSe on Si(111)7x7 results in formation of a pseudomorphic bilayer, which passivates the substrate dangling bonds and serves as the interface for further film growth. Component-resolved photoelectron diffraction (PED) and low-energy electron diffraction show this bilayer is oriented in a single domain, with the Ga-Se bond aligned with the substrate Si-Si bond. Combining scanned-angle and scanned-energy PED with theoretical calculations reveals the Ga and Se atomic positions. Ga sits directly atop surface Si, and the resultant interface bonding leaves Se lone-pair states on the surface. This makes the Si(111):GaSe surface highly resistant to contamination, and even additional GaSe does not stick for T@sub substrate@@>=@550°C. The measured PED patterns of Ga and Se 3d states show strong forward focusing along Ga-Se bond as well as diffraction rings from in-plane Se-Se scattering. The Ga-Se bond angle is between that for layered GaSe and cubic Ga@sub 2@Se@sub 3@. PED also shows strong (>20%) angular variation of the Ga3d spin-orbit branching ratio, while the Se 3d branching ratio is constant within 5%. This is likely associated with differences in photoionization matrix element and propogation of 3/2 and 5/2 states for the different local environments. * Supported by NSF DMR9801302.

11:20am **SS1+EM-TuM10 An Example of a Compound Semiconductor Surface that Mimics Silicon: The InP (001) (2x1) Reconstruction**, ***L. Li,*** *Q. Fu, B. Han, M. Begarney, D. Law, C. Li, R.F. Hicks,* University of California, Los Angeles

An InP (001) (2x1) reconstruction was prepared by metalorganic vapor-phase epitaxy. Scanning tunneling micrographs and infrared spectra of adsorbed hydrogen revealed that the (2x1) is terminated with a complete layer of buckled phosphorous dimers, giving rise to p(2x2) and c(4x2) domains. A surface band gap of 1.2 ± 0.2 eV was measured by scanning tunneling spectroscopy. The buckling can be explained by electron correlation among the dangling bonds of pairs of phosphorous dimers. This allows the surface to achieve a lower energy, semiconducting state. This reconstruction mimics the Si (100) (2x1), which is terminated with buckled silicon dimers.

11:40am **SS1+EM-TuM11 STM Studies of Sulfur Passivated InP(100)**, ***G.P. Lopinski,*** *R.A. Wolkow,* National Research Council, Canada; *C.D. MacPherson,* Nortel Networks, Canada

While sulfur passivation of InP(100) has been extensively studied by a number of techniques the details of the surface structure are still not definitively established. In this work we report STM studies of sulfur passivated InP(001) surfaces, prepared by wet chemical treatment in ammonium sulfide followed by annealing in UHV. Although the as prepared surface is disordered due to the presence of excess sulfur, highly pitted terraces evolve for annealing temperatures above 300C. Further annealing to 450C results in emergence of atomically flat terraces. LEED observations indicate the existence of a (3x1) phase in addition to the previously reported (2x1) structure. Atomically resolved STM images reveal the coexistence of local (3x1) and (2x1) periodicity. These surfaces are found to be stable with respect to brief air exposures.

Surface Science Division
Room 607 - Session SS2-TuM

Model Catalysts

Moderator: A.G. Sault, Sandia National Laboratories

8:20am **SS2-TuM1 The Microscopic Mechanism of Methanol Synthesis over the Zn-promoted Cu(111)**, ***J. Nakamura,*** University of Tsukuba, Japan; *I. Nakamura,* National Institute for Resources and Environment, Japan; *H. Nishimura, H. Nakano, M. Sano,* University of Tsukuba, Japan; *T. Fujitani,* National Institute for Resources and Environment, Japan

We had reported that the Zn-deposited Cu(111) could be regarded as a model of Cu/ZnO catalysts in terms of the turnover frequency of methanol formation and the activation energy. After establishing the catalyst model, we had further tried to look into the detailed mechanism on the promotional role of the Zn as well as the microkinetics using in-situ IRAS, XPS and STM apparatuses connected to a high pressure reactor. Very reactive formate species adsorbed in an inclined bidentate state was detected by IRAS, which was found to be responsible for the promotional effect of the Zn. Also the microkinetic picture was established for formate synthesis and formate decomposition. Interesting relationships between the ordered structure of formate observed by STM and the kinetics of decomposition were shown. That is, various ordered structures of formate intermediates synthesized from CO@sub 2@ and H@sub 2@ at 1 atm were very different from the structure of formate prepared by adsorption of formic acid, which cause a difference in the pre-exponential factor of the rate constant for the formate decomposition. This was explained by that a nearest neighbor formate species interfered with the OCO plane vibration of formate, which is probably necessary to overcome the transition state of the decomposition. The STM images of the Zn-deposited Cu(111) showed that Zn atoms were substituted for Cu atoms, leading to a Cu-Zn surface alloy. Upon the deposition of Zn, the alloying started at the step edges of the Cu(111) surface, and then the Zn atoms migrated toward the terrace. The migration rate was measured by time-resolved STM.

8:40am **SS2-TuM2 Vacuum and Electrochemical Characterization of a Model Pt(111) Catalyst Modified with Vapor-deposited Ru***, **D.S.W. Lim**, T.H. Madden, V.K. Medvedev, E.M. Stuve,* University of Washington*; T.J. Jarvi,* United Technologies Research Center

A practical liquid fuel cell anode catalyst must oxidize fuel in the presence of adsorbed carbon monoxide (CO), whether the actual fuel is methanol in the direct methanol fuel cell, or hydrogen from reformed hydrocarbons. While platinum (Pt) exhibits the greatest reactivity for fuel oxidation, it alone is unable to oxidize CO at potentials low enough to be practical. Pt modified with ruthenium (Ru) can however oxidize CO at lower potentials, although the details of the Ru enhancement have not yet been established. Also, the lack of reproducible performance of both model and industrial Pt / Ru fuel cell catalysts indicates that the preparation / processing effects on catalyst structure and performance have not been adequately assessed. In this work, a Pt(111) surface is modified with Ru via physical vapor deposition and characterized in ultra-high vacuum using AES, LEED, and TDS. The crystal is then transferred directly to an electrochemical cell where blank and methanol-oxidation voltammetry are performed. Early results using an industrial electron-beam Ru deposition source suggest simultaneous multi-layer growth of the Ru adlayer on Pt(111) at room temperature. Room temperature blank voltammetry indicates new features in the low-potential region due to Ru on Pt(111). Methanol-oxidation voltammetry indicates reduced peak currents due to lack of dissociative adsorption of methanol on surface Ru at room temperature. These electrochemical characteristics due to Ru on Pt(111) can largely be reversed by a mild 300 deg C anneal in vacuum. We recently developed a small electron-beam Ru deposition source in our lab which allows highly precise Ru deposition under good vacuum conditions. More detailed vacuum and electrochemical characterization using this source for the Ru / Pt(111) system will be discussed. This work was supported by the Office of Naval Research, the National Science Foundation, the Link Foundation, and the University of Washington.

9:00am **SS2-TuM3 Structurally Ordered Magnesium Vanadate Model Catalysts for Oxidative Dehydrogenation***, **A.G. Sault**, J.A. Ruffner,* Sandia National Laboratories

A fundamental understanding of the nature of the active sites in mixed metal oxide oxidation catalysts has proven elusive. The complex nature of these materials makes fundamental studies of active sites difficult. The use of single crystal surfaces to overcome this complexity is limited by the insulating nature of oxides, which restricts the use of many surface analytical probes. For simple oxides, some researchers have used ultrathin epitaxial oxide films to overcome these problems. Such films allow STM studies that provide unprecedented atomic detail regarding metal oxide surfaces. We are employing similar methods to study mixed metal oxide surfaces. Using RF sputter deposition, we have grown thin (<85 Å) films of Mg@sub 3@(VO@sub 4@)@sub 2@, a known selective oxidative catalyst. Bulk and surface analysis of films grown on Si wafers show the desired stoichiometry. By depositing Mg@sub 3@(VO@sub 4@)@sub 2@ on a 500 Å Au layer grown on an oxidized Si wafer, films strongly orientated in the (042) plane of Mg@sub 3@(VO@sub 4@)@sub 2@ can be grown. This plane consists of close packed oxygen layers, with Mg and V ions in octahedral and tetrahedral sites, respectively. Heating the films above 623 K in vacuum or 100 Torr propane results in partial reduction of V(V) to V(IV) and segregation of V to the surface. Treatment in oxygen reverses these changes. This reversible redox chemistry is consistent with the known mechanism for catalytic oxidation, which involves participation of lattice oxygen. We will report STM images of these surfaces, and detail the effects of heat treatments in reactive environments (e.g., oxygen/propane mixtures) on the structure and composition of these films. The formation of defects such as oxygen vacancies will be of special interest as lattice oxygen plays an important role in catalysis over mixed metal oxides. Through these studies we hope to provide the first detailed atomic scale view of active sites in this important class of catalysts.

9:20am **SS2-TuM4 The Atomic-scale Structure of MoS@sub 2@ Nano-cluster Catalysts Studied by STM***, **S. Helveg**, J.V. Lauritsen, E. Laegsgaard, I. Stensgaard,* University of Aarhus, Denmark*; B.S. Clausen, H. Topsoe,* Haldor Topsoe Research Laboratories, Denmark*; F. Besenbacher,* University of Aarhus, Denmark

Hydrodesulfurization (HDS) catalysis has recently attracted an increased interest partly augmented by the new severe environmental legislation. The activity of the industrial HDS catalysts has uniquely been related to the edge structure of MoS@sub 2@ nano-crystals. However, very little is known about the actual shape of the nano-crystalline MoS@sub 2@ particles and the exact edge structures. To obtain such structural insight, we have prepared a model system of 30 Å wide MoS@sub 2@ nano-clusters dispersed on the Au(111) model surface. High resolution Scanning Tunneling Microscopy (STM) studies unequivocally reveal that the MoS@sub 2@ nano-clusters are of triangular shape, and from atomically resolved STM images of the edge structures, we tentatively conclude that the edges are S restructured Mo terminated edges.

9:40am **SS2-TuM5 Linking Surface Science and Catalysis***, **I. Chorkendorff**,* Technical University of Denmark, DENMARK **INVITED**

Surface Science has in the past provided much of the framework and tools for understanding heterogeneous catalysis. Nevertheless, the pressure and structure gap still continues to provide unforeseen and interesting phenomena, which are necessary prerequisites in order that real catalytic processes under high-pressure conditions can be understood and modeled. It is therefore mandatory to identify which reaction pathways are prevailing and what structure and composition are present at increased pressure. In a number of examples it will be demonstrated how, by combining in situ high pressure experiments on well defined single crystals with DFT calculations, it is possible to gain a further insight in this direction. For example is it well known from UHV experiments that steps or defects may influence the surface reactivity substantially, but the influence on catalytic process have been of more speculative nature. It will be shown, how steps and/or defects increases the sticking of N@sub2@ on Ru(0001) by 8 to 9 orders of magnitude!! Since this is the rate-limiting step in the ammonia synthesis on Ru, it will naturally have a profound impact on the understanding of the ammonia synthesis, which was also studied. Turning to model system for alloy catalyst it will be demonstrated how the surface composition and availability for performing chemical reaction can be strongly dependent on gas induced segregation phenomena. A brief overview of the determining parameters will be given showing that the surface composition of alloys is dynamically dependent on temperature and the chemically potential of the gasses involved and cannot in many cases be determined from UHV experiments alone.

10:20am **SS2-TuM7 Flow Reactor Studies of Nanofabricated Model Catalysts; Activity and Reconstruction***, **S. Johansson**, E. Fridell, B. Kasemo,* Chalmers University of Technology, Sweden

Nanofabrication of model catalysts using the electron-beam lithography technique offers a way to produce geometrically well-defined model catalysts. Component interaction, particle separation and particle size (in the 10 nm range) can be controlled. Multi-layer structures can be obtained by repeating the fabrication-process. Furthermore, re-structuring can be accomplished by heat treatment afterwards in different gas mixtures. These nanofabricated catalysts are well suited to study, e.g., spillover effects in catalytic systems. A micro-reactor for catalytic evaluation of these nanofabricated model catalysts has been designed. It operates at atmospheric pressure and allows samples with a small total active surface area (below 1 mm@super 2@). This implies small gas-flows in the order of approx. 1-10 mm@super 3@/s. The small active surface-area comes from a limitation in the electron-beam lithography process to make large numbers of small structures in a reasonable time, due to the serial processing. The minimum Pt-surface-area needed for catalytic activity evaluation has not yet been determined for this system. Differences in the CO-reaction rate in the kinetically controlled region is measured as a function of interaction length between Pt and CeO@sub x@, where the total surface area of Pt has been kept constant. Morphology changes of nanofabricated Pt-discs with diameters up to 700 nm has been studied. Structural changes occur in reactant mixtures, e.g., CO+O@sub 2@ in Ar, at elevated temperatures

(500Â°C). Disintegration of the larger Pt-discs into several smaller crystalline Pt-particles is observed.

10:40am **SS2-TuM8 Increasing the C-O Bond Anharmonicity of Methoxy on Cu(100) with Coadsorbates**, *J.M. White, **H. Ihm**, K.C. Smith, H. Celio,* University of Texas, Austin

The C-O bond ahnarmonicity of methoxy induced by coadsorbates on Cu(100) has been studied using reflection absorption infrared spectroscopy (RAIRS). The analysis of the anharmonicity was carried out through the IR spectrum of a localized two-phonon bound state, the 2@nu@'@sub C-O@ excitation. For methoxy without coadsorbates, the vibrational frequencies of the C-O stretching mode and its overtone exhibit large coverage dependent shifts caused by dipole-dipole interactions. The anharmonicity of the C-O bond is @omega@@sub e@@chi@@sub e@=8.5 cm@sup -1@, which is 34% lower than that found for the gas phase methanol. Atomic oxygen markedly shifts the 2@nu@'@sub C-O@ band from 1951 cm@sup -1@ to 1940 cm@sup -1@, which consequently increases the anharmonicity by 11 cm@sup -1@. We have also compared results for methoxy from the thermal decomposition of methyl nitrite (CH@sub 3@ONO) on Cu(100) at different temperatures. We find that the 2@nu@'@sub C-O@ band can detect the presence of coadsorbed NO since the vibrational properties of the 2@nu@'@sub C-O@ band for both systems (methoxy-A-Cu(100) where A=O or NO) are quite similar. The definite correlation of the changes to the vibrational properties of methoxy induced by coadsorbates was achieved by using temperature programmed desorption (TPD) and Auger electron spectroscopy (AES).

11:00am **SS2-TuM9 Studies of the Oxidation Reactions of Methanol on a Heated Silver Membrane**, ***R.J. Beuhler**, R.M. Rao, M.G. White,* Brookhaven National Laboratory

A polycrystalline Ag-membrane is being used as a model substrate for investigating the kinetics and dynamics of Ag-catalyzed oxidation reactions, such as the epoxidation (EO) of ethylene and the partial oxidation of methanol. These Ag-catalyzed reactions are carried out on a large-scale commercially, and despite considerable effort to understand the reaction mechanisms, much still remains uncertain. We have been attempting to study these oxidation reactions under collision free conditions (pressures less than 10@super -5@ torr), allowing both electron impact mass spectroscopy and state-selective laser ionization techniques to be used for product analysis. The main advantage of the membrane is that high surface coverages of adsorbed O@sub (a)@ can be prepared by diffusion of oxygen atoms produced by dissociative adsorption at the high pressure side of the heated Ag foil. The oxygenated Ag-foil is found to be very active in promoting the partial oxidation of methanol to formaldehyde. At a methanol pressure of 10@super -6@ torr, the reaction rate is on the order of 10@super 15@ molecules/cm sec@super 2@, with a measurable lower limit of about 5 x 10@super 13@ molecules/cm sec@super 2@. During the initial heating of the foil, activation of the surface is observed. In complementary studies, O 1s XPS measurements have been performed on the Ag-foil surface to identify the chemical state of the adsorbed oxygen, and (2+1) REMPI laser spectroscopy has been used to extract ro-vibronic and velocity distributions for desorbed molecular oxygen formed by the recombination reaction O@sub (a)@ + O@sub (a)@ = O@sub 2(g)@.

11:20am **SS2-TuM10 Improved Catalytic Activity and Selectivity by Photon Irradiation**, *D. Chakarov,* Chalmers University of Technology and University of Göteborg, Sweden*; S. Ljungström,* Competence Centre for Catalysis, Sweden*; J. Bergeld, D. Ingert, V.P. Zhdanov, **B. Kasemo**,* Chalmers University of Technology and University of Göteborg, Sweden

Photo-catalysis is the enhancement of a chemical reaction by combined action of a catalyst and photons, on the reaction rate and/or selectivity. In heterogeneous photo-catalysis, the reaction occurs on a solid surface, with the reactants in gaseous or fluid state. The photons usually excite hot (photo) electrons that by transient attachment to one of the reactants enhance the reaction. In the present work, we explore the possibilities to increase the efficiency of catalytic emission cleaning by photo-catalysis. The approach includes both experimental and theoretical studies of the different parameters that may influence the photo-catalytic reactions, such as catalyst composition and wavelength dependence. The experiments are performed with conventional noble metal car exhaust catalysts at atmospheric pressure, nanofabricated model catalyst, and extended single crystals at UHV. Theoretical treatment includes studies of hot electron excitation-transport-attachment processes and Monte Carlo simulation. We present results concerning the reaction kinetics and light-off behavior for different CO + O2 and CO + NO mixtures on different catalysts. The main observations to date are: The light-off temperature can be reduced substantially (by up to 80 degrees) by photon irradiation at 365 nm. The single photon, non-thermal origin of this photocatalytic effect is confirmed by power- and wavelength- dependence measurements. The different characteristics of the photocatalysis on supported platinum, compared to single crystal Pt (111) in UHV, are discussed in terms of case specific adsorbate coverages, hot electron excitation, and reaction mechanisms.

11:40am **SS2-TuM11 Direct Observation of Propylene Transformation Chemistry on and in the Pores of Silver Exchanged Faujasite Catalyst**, ***S. Sambasivan**,* Brookhaven National Laboratory*; D.A. Fischer,* National Institute of Standards and Technology*; A. Kuperman,* Dow Chemical Company*; B.M. DeKoven,* Intevac Inc.

For the first time Near-Edge Soft X-ray Absorption Spectroscopy Fine Structure (NEXAFS) electron yield (surface sensitive about 50 Å) and fluorescence yield (bulk sensitive) have been applied simultaneously to characterize the adsorbed state of propylene in the surface and the bulk of the silver exchanged faujasite (LZY-52) catalyst. This technique is non-destructive, element specific, and a direct probe of the bonding and concentration of the adsorbed species, and reactive intermediates on a highly complex zeolite catalyst. Propylene adsorption on Ag/LZY-52 faujasite at 125 K showed that a bulk adsorbed state was a weakly interacting gas-phase like species with a highly intense carbon 1s to @pi@ *intensity which begins to desorb upon heating from 150 K to 300 K. On the other hand the propylene adsorbed on the surface forms a strongly chemisorbed intermediate with a small of carbon 1s to @pi@ * intensity but a strong @sigma@ * intensity indicating a formation of a sigma complex which is stable up to 250 K. A very small adsorption of propylene was observed on a zeolite with similar cage structure, high Si/Al ratio and no silver loading. The difference in the nature propylene adsorption in the bulk and surface of Ag/LZY-52 is discussed with respect to the difference in acidity and the size of the Ag particles in the surface and bulk zeolite. The NEXAFS technique is demonstrated as a practical new probe of molecular level reaction chemistry in catalyst materials.

Thin Films Division
Room 615 - Session TF-TuM

Advanced Thin Film Formation Chemistry

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

8:20am **TF-TuM1 Coatings from Liquid and Supercritical Carbon Dioxide**, *B.J. Novick, E.N. Hoggan,* North Carolina State University*; D. Flowers,* University of North Carolina*; Y. Chernyak,* North Carolina State University*; J.M. DeSimone,* North Carolina State University and University of North Carolina*; **R.G. Carbonell**,* North Carolina State University **INVITED**

Carbon dioxide offers several environmental as well as performance advantages over conventional solvents. The recent development of CO@sub 2@-soluble polymers and surfactants has broadened significantly the number of potential applications for supercritical and liquid carbon dioxide as a solvent for the formation of thin films and coatings. This paper discusses recent work on coatings of polymeric materials from both supercritical as well as liquid carbon dioxide. The rapid expansion of supercritical solution (RESS) process using CO@sub 2@ can produce thin films and sub-micron powders of a wide variety of inorganic and polymeric materials. The process involves the expansion of a solution through a nozzle to an ambient downstream pressure. The present work is aimed at gaining an understanding of the relationship between the morphology and dimensions of the precipitates and RESS operating conditions. A computational fluid dynamic analysis of the process path can help relate the rates of change of pressure and temperature in the nozzle to the thermodynamics of binodal and spinodal decomposition. These relationships govern deposition rates and the rates of droplet nucleation and growth. Liquid carbon dioxide also offers some advantages over conventional solvents for spin coating and free meniscus (dip coating) applications. Because of its low viscosity and low surface tension, it has the potential of forming thinner films and of penetrating into narrower features on the surfaces being coated. As examples, results are shown on the spin coating and development of CO@sub 2@-soluble polymers for photolithography, and the deposition of polymeric lubricants on the surface of hard disk drive materials by dip coating.

9:00am **TF-TuM3 Organic Films Prepared by Polymer Sputtering*, H. Biederman,*** Charles University at Prague, The Czech Republic, Czech Republic **INVITED**

Deposition of organic films by means of radio frequency (rf) sputtering of conventional polymers became the center of attention in the seventies. The interest was particularly in polytetrafluoroethylene (PTFE)@footnote 1@ because of the prospect to prepare useful dielectric films and low friction coatings. Recently the interest in polymer sputtering was renewed and in addition to PTFE polyimide (PI) and polyethylene (PE) etc. were examined.Findings from these studies are concisely reviewed. Recent results are presented from our laboratory, obtained using balanced and unbalanced rf magnetron sputtering of PTFE and PE. The results of the kinetics of rf magnetron sputtering of PTFE by energy resolved mass spectrometry are shown. Various C@sub X@F@sub Y@ species were detected in the discharge, with the composition affected by the discharge parameters. It is assumed that CF, CF@sub 2@ and CF@sub 3@ fragments from the sputter process are the most important for film growth.@footnote 2@ The process was also monitored in situ by OES (Optical emission spectroscopy). The morphology of fluorocarbon plasma polymer films deposited on Si substrates at various temperature was observed by means of scanning electron microscopy. It was concluded that below +23 °C a columnar structure appears. The structure and basic properties of hydrocarbon plasma polymer films prepared by rf sputtering of PE are presented. @FootnoteText@ @footnote 1@ Biederman, H , Ojha, S M, and Holland, L:Thin Solid Films, Vol 41, pp 329- 339, 1977 @footnote 2@ Zeuner, M, Hirsch, D, Neumann, H, Zalman, J and Biederman, H, to be published in Proc. of ISPC 14, Prague August 2-6,1999 .

9:40am **TF-TuM5 Plasma Enhanced Atomic Layer Deposition of Ta for Diffusion Barrier Applications***, A. Sherman,* Sherman and Associates, Inc.*; S. Malhotra,* ***S.M. Rossnagel,*** IBM Research Division

Atomic Layer Deposition (ALD) is a variation of conventional CVD that uses sequential steps for the adsorption of a monolayer of one reactant and the subsequent exposure of this monolayer to a second reactant, which results in the deposition of roughly a monolayer of the desired elemental or molecular species. This paper describes the use of a free radical second reactant which is produced by a remote plasma source. Because of the high reactivity, it is possible to form films at moderate temperatures rather than the high temperatures of conventional CVD. In this paper, we describe the ALD of Ta, which is used in semiconductor interconect structures for diffusion, adhesion, or nucleation layers in high aspect ratio features which are subsequently filed with Cu. The ALD process is self-limiting in that each 2-step process results in approximately a single atomic layer and film thickness is built up in a controlled manner with a specific number of steps. This is unlike conventional CVD or PVD which are generally timed and require rate calibration. The Ta system uses moderate temperature adsorption of TaCl5 vapor followed by a reaction step using atomic hydrogen from an inductively-coupled rf plasma. The system has been extended to 200mm wafers using a modified Applied Materials Endura (PVD) system, compatible with existing manufacturing tools. Conformal Ta films with uniform thickness have been measured in high aspect ratio features and XRD, AES and RBS data sugget films of high purity adequate for interconnect applications.

10:00am **TF-TuM6 Atomic Layer Deposition of Tungsten and Tungsten Nitride Using Sequential Surface Reactions***,* ***J.W. Klaus,*** *S.J. Ferro, S.M. George,* University of Colorado, Boulder

The deposition of ultrathin and conformal films on high aspect ratio structures is important for forming conducting layers and diffusion barriers. Thin films of tungsten (W) and tungsten nitride (W@sub 2@N) were deposited with atomic layer control using sequential surface reactions. The tungsten growth was accomplished by separating the binary reaction WF@sub 6@ + Si@sub 2@H@sub 6@ --> W + 2SiHF@sub 3@ + 2H@sub 2@ into two half-reactions. The tungsten nitride growth was performed by dividing the binary reaction 2WF@sub 6@ + NH@sub 3@ --> W@sub 2@N + 3HF + 9/2F@sub 2@ into two half-reactions. Successive exposure to WF@sub 6@ and Si@sub 2@H@sub 6@ (NH@sub 3@) in an ABAB... binary reaction sequence produced W (W@sub 2@N) deposition at substrate temperatures between 425-600 K (600-800K). The W deposition rate was 2.49 Å/AB cycle for WF@sub 6@ and Si@sub 2@H@sub 6@ reactant exposures > 800 L and 1600 L, respectively. The WN deposition rate was 2.55 Å/AB cycle for WF@sub 6@ and NH@sub 3@ reactant exposures > 3000 L and 10,000 L, respectively. Atomic force micrographs of the deposited films on Si(100) were remarkably flat indicating smooth and conformal deposition. These results for W represent the first demonstration of atomic layer deposition of conformal single-element films using sequential surface reactions. Similar surface chemical strategies may facilitate the atomic layer growth of other metals besides tungsten.

10:20am **TF-TuM7 Relating Phase Content to Deposition Kinetics in Ultra-Thin Sputtered Tantalum Films*, J.F. Whitacre,*** University of Michigan*; Z.U. Rek,* Stanford Synchrotron Radiation Laboratory*; S.M. Yalisove, J.C. Bilello,* University of Michigan

How phase and stress formation relate to adatom kinetics in extremely thin sputtered Ta films was examined. This was accomplished by controlling the adatom kinetic energy distribution at the substrate during growth. If low sputter gas (Ar) pressures are used (less than 5 mTorr), arriving adatoms have kinetic energies on the order of 10 eV as they impinge upon the substrate. At pressures above 15 mTorr, the energy distribution shifts to the thermal regime, where all atoms have energies less than 1 eV. For this experiment, Ta films 25 to 500 Å in thickness were DC magnetron sputter deposited using Ar pressures ranging from 2 to 20 mTorr. The films were analyzed using a synchrotron x-ray source (SSRL beamline 7-2) in conjunction with a four-circle diffractometer aligned in the grazing incidence x-ray scattering (GIXS) geometry. The stress in these films was calculated using double crystal diffraction topography (DCDT, a wafer curvature method) data. Film nanostructure was examined using TEM analysis. Phase content was determined by modeling ideal polycrystalline x-ray diffraction patterns and comparing them with corrected (for air scattering) diffraction data. It was found that films grown at progressively higher pressures displayed a systematic increase in amorphous content. Film grown using 20 mTorr of Ar were 100% amorphous to thicknesses as great as ~150Å. Residual stress analysis showed that all films less than 100 Å thick had compressive stresses on the order of -2 GPa. These results are discussed in context of a model that relates adatom kinetics, surface diffusion, and grain development during the early stages of film growth. Work supported by ARPA under contract No. DAAH-04-95-1-0120. Work done (partially) at SSRL, which is operated by the Department of Energy, Office of Basic Energy Sciences.

10:40am **TF-TuM8 Atomic Layer Controlled Growth of SiO@sub 2@ and Al@sub 2@O@sub 3@ on BN Particles Using Sequential Surface Chemistry*,*** ***J.D. Ferguson,*** *A.W. Weimer, S.M. George,* University of Colorado, Boulder

BN particles have a high thermal conductivity and are relatively inert. To improve BN particle coupling in polymer composites for thermal management applications, ultrathin coatings can be deposited that are more reactive and do not degrade the BN thermal properties. SiO@sub 2@ and Al@sub 2@O@sub 3@ were grown on BN particles with atomic layer control using sequential surface reactions of SiCl@sub 4@/H@sub 2@O@footnote 1@ and Al(CH@sub 3@)@sub 3@/H@sub 2@O,@footnote 2@ respectively. The sequential surface chemistry was monitored in vacuum using transmission Fourier transform infrared vibrational spectroscopy. The initial BN particles displayed B-OH and B-NH@sub 2@ surface species. These groups reacted with SiCl@sub 4@ or Al(CH@sub 3@)@sub 3@ and converted the surface species to Si-Cl or Al-CH@sub 3@. The subsequent reaction with H@sub 2@O converted the surface species to Si-OH or Al-OH. By repeating the sequential surface reactions, SiO@sub 2@ and Al@sub 2@O@sub 3@ bulk vibrational modes increased with number of reaction cycles. Transmission electron microscopy studies revealed conformal coatings on the BN particles. X-ray photoelectron spectroscopy analysis was also consistent with uniform and conformal deposition. These results illustrate the potential of sequential surface reactions to deposit conformal and atomic layer controlled coatings on particles. @FootnoteText@ @footnote 1@ J.W. Klaus, A.W. Ott and S.M. George, Appl. Phys. Lett. 70, 1092 (1997). @footnote 2@ A.W. Ott, J.W. Klaus and S.M. George, Thin Solid Films 292, 135 (1997).

Vacuum Metallurgy Division
Room 620 - Session VM+TF-TuM

Ionized Plasma and Chemical Vapor Deposition

Moderator: B. Sartwell, Naval Research Laboratory

9:00am **VM+TF-TuM3 New Plasma Sources for Ionized PVD*, D.N. Ruzic,*** University of Illinois, Urbana*; D.B. Hayden,* Novellus Systems Inc.*; D.R. Juliano, M.M.C. Allain,* University of Illinois, Urbana **INVITED**

Three plasma sources have been investigated on a commercial magnetron sputtering system: an inductively coupled plasma (ICP) coil, a helical resonator, and an external helicon antenna.@footnote 1@ The main variables presented are the ionization fraction to the substrate, the deposition rates, the electron density and temperature. The ICP coil with an Al target achieved ionization fractions to the substrate in excess of 80%. The deposition rates are around 1500 Å/min. Electron densities are found as high as 2.6±0.3 X 10@super 11@ cm@super -3@. The main drawback to the ICP approach is that the coil is too intrusive, leaving visible shadowing effects which destroy uniformity. The coil sputters some, and also flakes off built-up deposited metal, which can contaminate the system. The helical resonator coil has a much larger diameter and avoids the shadowing effects. Ionization fractions are found with a Cu target at 73±15% under conditions with deposition rates of 1000 Å/min. The electron densities approach 2. X 10@super 12@ cm@super -3@. A ground at the center of the coil eliminates the sputtering problem by maintaining a DC bias of 0~V. There is still metal flaking off the coil as metal builds up on it. The helicon antenna sits remotely outside the vacuum system, so all shadowing and contamination problems are eliminated. Cu ionization fractions to the substrate of 51±10 % with a deposition rate of 850 Å/min. are found using one remote source. The plasma density was only 2. X 10@super 11@ cm@super -3@, but the temperature of that plasma was significantly higher than without the remote helicon present. Six or more remote sources are envisioned to sit around a sputtering chamber, which can help control uniformity while increasing the ionization further. Since there is no threat of contamination inside the vacuum chamber and the substrate to target distance can remain small, the helicon source may have the highest potential of these three secondary sources in industrial IPVD applications. @FootnoteText@ @footnote 1@ D.B. Hayden, D.R. Juliano, M.N. Neumann, M.M.C. Allain, D.N. Ruzic, "Helicon Plasma Source for Ionized PVD," Surf. Coating Tech., to be published (1999).

9:40am **VM+TF-TuM5 Simulations and Experimental Measurements of a Hollow Cathode Magnetron Ionized Metal Plasma Deposition System***, **G.I. Font**, K.F. Lai, Q. Lu,* Novellus Systems, Inc.*; M.J. Kushner,* University of Illinois, Urbana

The hollow cathode magnetron (HCM) is a novel new plasma source used for ionized metal deposition. The HCM employs geometric, electrostatic, and magnetic confinement to produce a high density plasma (>1e+12 #/cm3). This plasma serves as a source of ions for sputtering the target and metal ions for deposition on a wafer. In the results reported here, numerical simulations of the HCM using a copper target were performed using the Hybrid Plasma Equipment Model (HPEM) developed at the University of Illinois. The HPEM iteratively combines particle and fluid transport models for ions, electrons, and neutrals to simulate HCM performance. The model includes sputtering of the target by metal and argon ions, secondary electron emission, magnetic confinement of electrons, and thermalization and ionization of sputtered neutrals. The numerical results are compared with experimental Langmuir probe and wafer deposition profile measurements. The numerical results are found to systematically track the experimental measurements. In both experiments and modeling of an HCM, the magnetic field configuration resulted in a confined 'beam' of plasma emanating from the HCM. The physics of the operation of the HCM is described as supported by numerical and experimental results.

10:00am **VM+TF-TuM6 Low Temperature Polysilicon Deposition by Ionized Magnetron Sputtering***, **J. Joo,*** Kunsan National University, Korea

Ionized PVD has deep potential for wide range of applications in thin film deposition. Poly Si deposition on glass should be one of them. A-Si based TFT technology has a limit of electron mobility less than 1 cm@super 2@ V/sec. Excimer laser annealing would be one solution for recrystallization but too expensive and slow process in economic point of view. As Si has very high melting temperature, the required substrate temperature for crystallization is well over the softening temperature of conventional glass in flat panel industry. RF ICP based ionized magnetron sputtering was applied to deposit polysilicon on glass substrate while keeping substrate temperature less than 400C. From X-ray diffraction analysis, small evidence for microcrystalline Si was confirmed at 250C of substrate temperature and floating substrate potential. The effects of pulsed dc sputtering power, substrate biasing frequency and ICP driving frequency will be addressed in detail.

10:20am **VM+TF-TuM7 A Study of the Mechanical Behaviour of Plasma Deposited Silica Films on Polycarbonate and Steel***, A. Hofrichter, A. Constantinescu,* CNRS, Ecole Polytechnique, France*; S. Benayoun,* E.N.S.A.M, France*; P. Bulkin, **B. Drévillon,*** CNRS, Ecole Polytechnique, France

The deposition of silica for protective coatings on polymers is of increasing interest for various applications. Key issues in the mechanical behaviour of the film are the properties of the film-substrate interface that can be modified by different pretreatments. The objective of this work is to estimate the constitutive behaviour of the film and the interface by a serie of mechanical experiments and computer simulations. In order to gain a better understanding of the involved phenomena a comparison between depositions on polycarbonate and stainless steel have been performed. The films are deposited in a low pressure (1 mTorr), scaleable integrated distributed microwave 2.45 GHz electron cyclotron resonance (IDECR) reactor, which allows fast deposition at room temperature of dense, stoechiometric silica. The internal stress of the films was evaluated with profilometry and their Young modulus measured by the vibrating slab technique. Microscratch as well as nano-, micro- and Vickers indentation tests were performed on polycarbonate and steel samples for different thickness and processing powers. As indentation measurements can not be interpreted directly, the tests have been simulated by finite elements using the Castem2000 code (CEA-France). The simulated indentation curves and the final shape of the indent were compared to the measurements. The obtained stress and strain distribution in the film conducts to a reasonable explanation of the crack system observed on the indented surfaces. Finally a parametric study of the influence of the material parameters of the interlayer on the global mechanical behaviour will also be presented.

10:40am **VM+TF-TuM8 Carburizing of Tantalum by Radio-Frequency Plasma Assisted CVD***, A. Rubinshtein,* Ben-Gurion University*; **A. Raveh,*** NRC-Negev, Israel*; J.E. Klemberg-Sapieha, L. Martinu,* Ecole Polytechnique, Canada

Tantalum carbide has a great potential as an alternative to tantalum and tantalum oxide for applications requiring thermal stability and corrosion resistance. In the present work we are studying hard TaC layers prepared by inductive rf plasma-assisted CVD (IPACVD) in different gas mixtures containing argon, methane, and hydrogen. The IPACVD approach combines plasma-induced diffusion with chemical vapor deposition. Maximum temperature of the tantalum substrate measured during 6 hours of processing time was 900 degC. Microstructure of the TaC layers was characterized by XRD, AFM, AES, and XPS, and the mechanical properties were studied by micro- and nanoindentation techniques. Close correlation between carburizing parameters, microstructure and mechanical properties of the layers has been established. The best mechanical performance in terms of elasto-plastic properties (microhardness of about 25 GPa) were obtained for several micrometers thick TaC films prepared at rf power levels between 1.6-2.0 kW and pressures between 40 and 60 mTorr. The effect of gas composition, rf power and substrate temperature on the layer composition (TaC/Ta@sub 2@C phase ratio), and the mechanical behavior will be presented and discussed.

11:00am **VM+TF-TuM9 Electrical and Pressure Probe Measurements of a Hollow Cathode Magnetron Plasma***, **K.F. Lai**, Q. Lu, J. Chau, G.I. Font,* Novellus Systems

The hollow cathode magnetron (HCM) is a new type of high-density plasma device developed for ionized physical vapor deposition (I-PVD). While I-PVD using RF inductively coupled plasma has a plasma density of 10@super 11@ to 10@super 12@ cm@super -3@ and operates best above tens of mTorr, the HCM achieves high levels of ionization at only a few mTorr, primarily due to its extremely high plasma density (~10 @super 13@ cm@super -3@). The plasma profiles of a HCM were measured using Langmuir probes and a novel pressure probe under various operating conditions for two different target materials (Cu and Ti). With the exception of the plasma edge where the presence of an energetic electron tail was clearly evident, the electron energy distribution function (EEDF) was approximately Maxwellian. The measured plasma density was found to increase linearly with the magnetron power whereas the electron temperature only has a weak dependence. Under similar operating conditions, the Ti HCM has a plasma density ~30% higher than that of Cu. A novel pressure probe was used to measure both the argon neutral and ion density profiles. Argon neutrals were measured when the probe was biased slightly above the plasma potential whereas both the argon neutrals and ions were collected when the probe was negatively biased. The percentage of gas rarefaction was found to increase with sputtering power but was only weakly dependent on argon density. The argon ion density profile (deduced by alternating the pressure probe bias) has similar shape as the electron density (measured by the Langmuir probe) indicating that argon is the dominant ion species. The experimental results are in good agreement with simulation using the hybrid plasma equipment model (HPEM) code.

Vacuum Technology Division
Room 610 - Session VT-TuM

Total and Partial Pressure Gauging

Moderator: Neil Peacock, MKS Instruments, Inc.

8:20am **VT-TuM1 Recommended Practice for Calibrating Vacuum Gauges of the Thermal Conductivity Type*, A.P. Miiller,*** National Institute for Standards and Technology*; R.E. Ellefson,* Leybold Inficon Inc.

Thermal conductivity gauges (TCGs) are used extensively in the pressure range of the order of 10@super -1@ Pa (10@super -3@ Torr) to atmosphere. This presentation summarizes the content of a recently completed Recommended Practice for calibration of thermal conductivity gauges. The recommended calibration hardware references capacitance diaphragm gauges as the transfer standard for a practical calibration gauge. The vacuum system and gas handling methods are also presented. The calibration methods recommended are similar to those used by manufacturers for factory calibrations of their TCGs. The expected accuracy of a TCG is in the range of 5 % to 20 % of reading. This recommended practice provides users with a method for their calibration as well as good practices for the use of these gauges in vacuum applications.

8:40am **VT-TuM2 The Use and Calibration of Spinning Rotor Gages at Non-Ambient Temperatures*, C.R. Tilford,*** National Institute of Standards and Technology, US*; B. Lindeanau,* FZJ-IGV, Germany

Many applications require accurate low pressure measurements at temperatures different from room temperature. These measurements are complicated by thermal transpiration effects and the thermal and chemical perturbations associated with most high vacuum gages. The use of an in situ spinning rotor gage (SRG) is a possible solution for such problems. The SRG is stable, inert, and its power disappation is in the milliwatt range. However, for the most accurate measurements it must be determined if the effective accomodation coefficient, the factor determining the sensitivity of the SRG, is temperature dependent. This talk describes the design and performance of a calibration system that corrects for thermal transpiration effects and allows the in situ calibration of SRGs for temperatures between 77 K and 400 K. This system has been used to investigate the temperature dependence of the effective accomodation coefficients for both "smooth" and deliberately roughened steel balls used as SRG rotors.

9:00am **VT-TuM3 Extension of the Spinning Rotor Gauge to Lower Pressure*, J.P. Looney,*** National Institute of Standards and Technology

The Spinning Rotor Gauge (SRG) is widely used for vacuum gauge calibration and measurement in the pressure range 0.1 Pa to somewhat below 10 @super -4@ Pa (10 @super -6@ Torr). The lower limit of presently available SRGs is due to essentially two factors (i) the ability to measure the rotor deceleration rate with a precision of better than about 10 @super -10@ s @super -1@ and (ii) large residual torques on the rotor. The first can be overcome by improved timing of the rotation rate of the ball and the second can be overcome by development of suspension heads with smaller residual torques on the spinning rotor. Together, a system can be constructed to make measurements to much lower pressures, perhaps below 10 @super -6@ Pa (10 @super -8@ Torr) with an imprecision of <1% for a four minute measurement interval. The factors which limit the useful pressure measurement range of the SRG will be dicsussed and initial performance measurements for a prototype system will be presented.

9:20am **VT-TuM4 Enhanced Bayard-Alpert Gauge with Accuracy and Stability Improved by Design and Construction*, P.C. Arnold,*** Granville-Phillips, Division of Helix Technology Corp. **INVITED**

An enhanced accuracy and stability Bayard-Alpert gauge, now in general use for over five years, is reviewed. The philosophy of its design to control electron trajectories, location of ion generation, efficiency of ion collection, and maintenance of these characteristics is described with respect to computer simulation and its resultant gauge construction. Gauge sensitivity variation with pressure, from gauge to gauge, and over five years of operation is presented. A system for multi-gauge calibration is described as well as the system for maintaining the reference standards. Analyzing commercial use of this gauge in process environments over these five years has revealed knowledge relating to degradation of the function of each gauge electrode. Also analyzed are the process cycle requirements of quickly measuring base pressure under process conditions versus backfilling to pressures well above base pressure. Many of these concepts are generally applicable to most ionization gauges and will be discussed.

10:00am **VT-TuM6 A Miniature Dual-Collector Ionization Gauge*, A.R. Filippelli,*** Granville-Phillips, Division of Helix Technology Corp.

In recent years there has been a trend to reduce the physical size of the sensors used in the semiconductor manufacturing industry. Because of the great utility of the Bayard-Alpert ionization gauge in this industry, it is natural for gauge manufacturers to ask: Can we retain its basic three-element design, operating voltages, good sensitivity, and low x-ray limit and, at the same time, significantly reduce its size? The answer is yes. This talk will introduce the basic concept that motivated a dual-collector design and will then trace the development of the miniature gauge based on this concept. Some details of the design were guided by use of a modeling program, and examples of ion and electron trajectories computed using this program will be shown. Experimental testing of prototypes, in conjunction with modeling, was used to select other design parameters such as filament length, collector diameter, and grid end geometry. Experimentally-determined test results for sensitivity and x-ray limit will also be presented. While no single design factor appears to dominate the gauge's performance, the combination of design choices has resulted in a gauge with good sensitivity as well as a significantly smaller size.

10:20am **VT-TuM7 A Compact Wide-Range Cold-Cathode Gauge*, B.R.F. Kendall,*** Elvac Laboratories*; E. Drubetsky,* The Fredericks Company

Cold-cathode ionization gauges offer many advantages for routine high-vacuum measurements. They are simple and robust. Thermal outgassing and electron-stimulated desorption, both significant problems in hot-cathode gauges, are negligible. There are no x-ray effects to cause errors at low pressures. New design techniques have largely eliminated stray-field and starting problems. The design, development and testing of a compact wide-range cold-cathode gauge are discussed. Demountable and all-metal versions have small internal volumes ranging from 5 to 15 cm@super 3@, yet the sensitivity can exceed 10A Torr@super -1@ at 10@super -6@ Torr. Double inverted magnetron geometry and shielding rings reduce the external magnetic fields to very low levels. The anode contains thorium for easier starting at normal pressures. For UHV applications, Americium 241 or a carbon film cold emitter can be used for instant starting. Test data are given which illustrate the effects of varying anode voltages and magnetic fields upon sensitivity and starting time. Factors affecting stability and freedom from discharge discontinuities are also discussed. Design features allowing stable operation down to 10@super -11@ Torr and above 10@super -2@ Torr are described.

10:40am **VT-TuM8 New Enhanced Performance Low Pressure Capacitance Manometer*, C.P. Grudzien,*** MKS Instruments

The measurement performance of low pressure capacitance manometers has traditionally been influenced to varying degrees by many factors including barometric pressure, ambient temperature change, shock, vibration, material creep and rapid pressure excursions. Many improvements and developments have occurred since the original capacitance manometer technology was invented over forty years ago. Previous capacitance manometer designs address several of these pressure independent influences, but in the process, trade off performance in other areas. A new enhanced performance design is described here that incorporates several unique approaches to reducing these influences and provides for a practical, robust platform. The unique radial 'spoke' geometry isolates the sensitive capacitance elements from unwanted body forces and thermal transients, yielding stable zero and span performance. Experimental data and computer simulation show that measurements using instruments with full scale ranges of 100 mTorr (~10 Pa) and below are superior to that of previous state-of-the-art methods. The enhanced performance capacitance manometer design establishes a basis for continual improvement and a path to meet the future requirements of the vacuum community.

11:00am **VT-TuM9 A Review of Thermal Transpiration Corrections in Capacitance Diaphragm Gauges*, J. Setina,*** Institute of Metals and Technology, Slovenia

Capacitance diaphragm gauges (CDGs) play important role in vacuum metrology because of their accuracy and resolution. They are widely used in calibration laboratories as reference and transfer standards for calibration of other pressure measuring devices in the pressure range from 0.01 Pa to 100 kPa. CDGs are inherently susceptible to ambient temperature variations. Operating CDGs at stabilised elevated temperature greatly improves the zero stability and enables relative resolution of few ppm of gauge full-scale but also introduces nonlinearities, which are known as thermal transpiration (TT) effect. In applications, where the uncertainty of measurements must be reduced to less than one percent, the response of CDG has to be corrected for TT effect if measured pressure is below 100 Pa. TT effect had been studied in detail by Takaishi and Sensui,@footnote 1@ and their empirical formulas are widely accepted for corrections of CDG measurements. In the present paper we will address the accuracy of this formulas which were published four decades ago. We have done some accurate calibrations of CDGs in the pressure range from 0.01 to 133 Pa in four gases: N@sub 2@, Ar, He and H@sub 2@. For He we found discrepancy of our data from Takaishi and Sensui empirical formula as large as 0.3 % in the range of pressures from 0.5 to 5 Pa. Scaling of thermal transpiration curves for different gases with the inverse of Knudsen number was also observed. This has not been reported by other authors. Vacuum metrology greatly advanced since the work of Takaishi and Sensui. The improvement in measurement accuracy at primary laboratories in the past ten years allows much more precise measurements in the range from 0.01 to 100 Pa. Therefore we suggest a thorough re-evaluation of the TT effect that should include a variety of gases with which CDGs are commonly used as well as the influence of momentum exchange of gas molecules on the surface of the tube that connects a CDG to the vacuum system. @FootnoteText@ @footnote 1@ Takaishi T., Sensui Y.,Trans.Faraday Soc., 1963, 59, p. 2503

11:20am **VT-TuM10 Partial Pressure Analyzers in the Relativistic Heavy Ion Collider***, **L.A. Smart**, D. Loughlin, R.J. Todd, R.C. Lee,* Brookhaven National Laboratory

The Relativistic Heavy Ion Collider (RHIC) at Brookhaven National Laboratory incorporates large-scale high and ultrahigh vacuum systems. Partial pressure analyzers (PPAs) are employed to monitor the gas composition of these volumes remotely. PPAs with faraday cup detectors are placed along cryostat vessels that are up to 480 meters long. Data trends in both displacement and time are used to indicate helium or air leaks into the system and their probable locations. Electron multiplier units are employed to peer into the ultrahigh vacuum beam chambers near the interaction region detectors, where beam-on-beam collisions occur. The acquisition, testing, installation and control of the PPAs will be discussed with a summary of the system performance in the first few months of RHIC operation.

11:40am **VT-TuM11 The Modern and Flexible Upstream Controller***, **H.-Ch. Gehlhar,*** Leybold Inficon, Liechtenstein

The modern vacuum applications ask more and more for constant pressures in chambers and reactors or constant gas flow to maintain certain atmospheres in those chambers. This can be done in different ways, e.g. downstream control, massflow control or as we would like to discuss now by upstream control. A very simple version of upstream control could be a limit switch controlled valve operation by just opening or closing the valve. A simple and inexpensive method with all pros and cons concerning any system requirement. As an improvement to this, modern upstream controllers are flexible and give various opportunities to justify the pressure control circle in a vacuum system. The parameters to take care of like: chamber size, pumping speed, response times, time requirements etc. are very well known by everyone who has ever designed such a control circle. The user requirements of the vacuum system combined with all these parameters result in a level of requirements of a controller and a valve as well as for the applied gauges. Those requirements may vary in such a wide range that many pressure controllers are by far out of their limits. Modern solutions for pressure controllers or upstream controllers may not cover every extreme requirement. These new and advantageous controllers give flexibility in choosing out of various gauges and allow to justify the PID parameters in a wide range that nearly most of the known applications are covered in a satisfying way.

Applied Surface Science Division
Room 6A - Session AS-TuA
Modeling in Applied Surface Science

Moderator: C.S. Fadley, Lawrence Berkeley National Laboratory

2:20pm **AS-TuA2 A Microscopic View of Energetic Desorption Events***, **B.J. Garrison**,* Pennsylvania State University **INVITED**

Molecular dynamics computer simulations have been used to model desorption processes of energetic particle bombardment (SIMS, FABMS) as well laser ablation of organic films (MALDI). The results of the simulations are used to compare with experimental data and to provide microscopic insight into the fundamental events. The particle bombardment examples to be discussed include energy and angular distributions of ejected metal atoms and benzene molecules, mechanisms of ejection of organic molecules, and bombardment by cluster projectiles. Topics to be discussed from the laser ablation studies include microscopic mechanisms of ablation, an analytic expression of the velocity distribution of the plume and conditions for desorption of large molecules as in MALDI experiments. Further information can be found at http://galilei.chem.psu.edu/.

3:00pm **AS-TuA4 Theory of Multi-Atom Resonant Photoemission***, **F.J. Garcia de Abajo**, C.S. Fadley, M.A. Van Hove,* Lawrence Berkeley National Laboratory

Multi-atom resonant photoemission (MARPE) takes places when a core electron of a solid can be excited by an incoming photon beam via two different channels: direct photoexcitation and resonant excitation of a nearby atom that decays via inter-atomic interaction giving rise to the emission of the same core electron. This process permits one to detect the presence in the sample of neighboring atoms A and B of different atomic identity by observing the photoemission signal coming from atom A when the photon energy runs across an absorption edge of atom B. MARPE has been recently observed in several materials, including alloys and multilayered surfaces. A theory of this phenomenon is described here showing good agreement with experiment.

3:20pm **AS-TuA5 Oxide-free Phosphate Films on Metals probed by Core and Valence Band X-Ray Photoelectron Spectroscopic Studies in an Anaerobic Cell***, J.A. Rotole, **P.M.A. Sherwood**,* Kansas State University

This paper will show how clean metal surfaces can be reacted via aqueous electrochemical treatment in an anaerobic electrochemical cell to yield a phosphate film that can be directly attached to the metal surface without the presence of any intervening oxide. Such oxide-free films have the potential to serve as a corrosion inhibiting film, and may have other applications such as in the formation of biocompatible surfaces. Previously published work on aluminum and iron will be discussed but the focus of the paper will be new studies on copper. The work illustrates how it is essential to start with an oxide-free metal surface and to perform the treatment in an inert environment in an anaerobic electrochemical cell using aqueous phosphoric acid. It will also be seen that valence band photoemission, interpreted by band structure and other calculations, is a very effective tool for conclusively identifying the surface species present, and in particular distinguishing between oxide and phosphate surface films. This material was based upon work supported by the National Science Foundation under Grant No. CHE-9421068.

3:40pm **AS-TuA6 Spatial Resolution in Scanning Auger Microanalysis of Complex Systems***, **A.L. Linsebigler**,* General Electric Corporate Research and Development Center

Auger electron spectroscopy is one of the primary surface analytical tools in industrial laboratories. The introduction of analytical instrumentation with field emission sources has expanded the capabilities of Auger analysis to include sub-micron phase and particle identification. The spatial resolution of scanning Auger microanalysis is always in question, especially for complex samples such as alloys and multi-component systems. The primary beam size, the primary beam voltage, and the material under investigation are some of the variables which limit the spatial resolution of Auger electron spectroscopy. This study examines the interfacial resolution of metal films with atomic number differences ranging from delta Z = 6 to 65 as a function of primary beam voltage. The interfacial resolution of practical samples such as intermetallic/metal and oxide/metal combinations are also examined. The experimental results will be compared to predictions made by Monte Carlo simulations of electron - solid interactions.

4:00pm **AS-TuA7 Atomic Level Characterization of Metal-Ceramic Interface Energetics and Dynamics via Ab Initio Methods***, **E.A. Carter**, A. Christensen, E. Asche,* University of California, Los Angeles **INVITED**

This talk will be divided into a progress report on ab initio theoretical methods that have been developed to characterize the behavior of interfaces at the atomic level followed by applications of first principles techniques to applied problems. First, w e will discuss a newly developed systematic and accurate theory of adsorption energetics on metals. Second, we will present calculations aimed at understanding the adhesion and ultimate spallation of ceramic coatings on metals. Thermal barrier coatings us ed in high temperature mechanical applications consist of ceramics that are generally spray-coated onto alloy metal surfaces. We will show how one can learn about the interfaces in such materials at the atomic level, via first principles electronic structure techniques. In particular, we will discuss results and insights gleaned from examining surfaces and thin films of ZrO2, Al2O3, their interactions with each other, as well as with Ni surfaces.

4:40pm **AS-TuA9 Surface Science Studies of Model Ziegler-Natta Polymerization Catalysts***, G.A. Somorjai, **S.H. Kim**,* University of California at Berkeley

Model Ziegler-Natta catalysts of titanium chloride, supported on Au and MgCl@sub 2@, have been synthesized using chemical vapor deposition (CVD) methods in a ultra-high vacuum (UHV) chamber and tested for polymerization of ethylene and propylene with triethylaluminum, AlEt@sub 3@, as a co-catalyst in a high-pressure reaction cell. The deposition kinetics, chemical composition, surface sites, and activation of model catalysts are investigated using Auger electron spectroscopy (AES), x-ray photoelectron spectroscopy (XPS), and temperature-programmed desorption (TPD). TiCl@sub 4@ does not chemisorb on either Au or MgCl@sub 2@ to form a film stable at room temperature in UHV. The titanium chloride films supported on Au (TiCl@sub x@/Au) are produced by electron beam irradiation onto the substrate during the TiCl@sub 4@ exposure. Electrons induce the ionization and dissociation of TiCl@sub 4@, producing active species that can be deposited on Au at both 100K and 300K. The deposition temperature alters the stoichiometry and structure of TiCl@sub x@/Au due to difference in deposition kinetics. The titanium chloride films supported on magnesium chloride (TiCl@sub x@/MgCl@sub 2@/Au) are prepared by reaction of TiCl@sub 4@ with Mg on Au. Two deposition sequences, co-deposition of gas-phase Mg and TiCl@sub 4@ and deposition of TiCl@sub 4@ on a Mg film, are used. Regardless of deposition sequence, the uppermost layers of the TiCl@sub x@/MgCl@sub 2@/Au films are mostly composed of titanium chloride, though the distribution of titanium chloride in the film changes with deposition sequence. For these model catalysts before and after the AlEt@sub 3@ treatment, desorption behaviors of organic molecules are studied to differentiate various adsorption sites on the surface. Identification of active sites for polymerization will be attempted from the comparison of the distribution of surface sites with polymerization activity.

5:00pm **AS-TuA10 Dynamic Monte Carlo Simulations of Catalytic Surface Reactions: CO + NO on Rhodium***, **J.W. Niemantsverdriet**, M.J.P. Hopstaken, J.J. Lukkien, A.P.J. Jansen, P.A.J. Hilbers,* Eindhoven University of Technology, The Netherlands

A Dynamic Monte Carlo simulation procedure which succesfully describes diffusion, adsorbate interactions, island formation and reconstructions, has recently been described.@footnote 1@ We have used this approach to describe adsorption, desorption and dissociation of NO, as well as reactions between CO and NO on Rh(111) and Rh(100). When NO is adsorbed on Rh(111), TPD shows that the saturation increases from 0.68 ML at 150 K to a 0.75 ML at 225 K.@footnote 2@ This is accompagnied by ordering of the adsorbate layer, as evidenced by LEED. These phenomena are accounted for by a delicate interplay between mobility of and lateral interactions between NO molecules. We have also used Monte Carlo techniques to simulate recent experimental results on NO adsorption at elevated temperatures, where NO adsorbs both dissociatively and molecularly. Static SIMS shows that dissociation starts at 250 K and continuously increases up to 350 K. These experimental observations are satisfactorily explained in the model by adding pairwise repulsive interactions between neighbouring adsorbed species, which increases the activation barrier for dissociation. Similar effects play a role in the explosive reaction between CO and NO on fully occupied surfaces. In addition to repulsive interactions, fast diffusion of adsorbed molecules appears to be essential to reproduce explosive behavior in the simulations. The key point is that for a realistic description of repulsion between adsorbates, one has to consider the local environment of an adsorbed atom or molecule. @FootnoteText@ @footnote 1@ R.J. Gelten, A.P.J. Jansen, R.A. van Santen, J.J. Lukkien, J.P.L. Segers, P.A.J. Hilbers, J. Chem. Phys. 108 (1998) 5921. @footnote 2@ R.M. van Hardeveld, M.J.P. Hopstaken, J.J. Lukkien, P.A.J. Hilbers, A.P.J. Jansen, R.A. van Santen, J.W. Niemantsverdriet, Chem. Phys. Lett. 302 (1999) 98.

Biomaterial Interfaces Group
Room 613/614 - Session BI-TuA

Characterization of Biomaterial Interfaces

Moderator: M. Grunze, University of Heidelberg

2:00pm **BI-TuA1 Surface Characterization of Biomaterials with Protein Layers**, ***H.J. Griesser,*** CSIRO Australia, Australia **INVITED**

In the fabrication and interfacial analysis of novel biomaterials and their biological interactions, vacuum-based methods occupy a prominent role. Much research centers on the fabrication of "hybrid" biomaterials, which comprise a synthetic carrier material and an immobilized layer of biologically active molecules. Low temperature gas plasma methods are well suited to the attachment of reactive chemical groups onto polymers. Alternatively, plasma polymer interlayers can be used to provide reactive surface groups for the covalent interfacial immobilization of proteins. Vacuum-based surface analysis techniques characterize the surface properties of a material and increasingly are applied to the study of interfacial interactions with biological molecules. In this talk I will present examples of recent work on the immobilization of proteins and synthetic peptides on polymers via plasma polymer interfacial bonding layers. Detailed, multitechnique characterization of surface derivatizations and protein immobilizations is essential since proteins can adsorb and thereby mimic an intended covalent immobilization. Intended attachments are first modelled using derivatization reactions, and the surface density of reactive groups is thus determined. MALDI mass spectrometry is uniquely suited to the detection of adsorbed biomolecules at amounts much below monolayer coverage, and this method has been used to distinguish between covalent and adsorptive immobilizations. MALDI-MS is also eminently suited to the study of which proteins adsorb from complex, multicomponent media. For instance, the ways in which different surface chemistries of contact lenses influence which proteins adsorb onto lenses worn by human volunteers, has been characterized by MALDI-MS, and this information is being used for the guided design of improved coatings. Finally, I will discuss how AFM in the force mode provides complementary information to vacuum-based analysis methods.

2:40pm **BI-TuA3 Surface-plasmon Field-enhanced Fluorescence Spectroscopy and -Microscopy for the Evaluation of the Hybridization Reaction of Oligonucleotides**, ***W. Knoll,*** Max-Planck-Institut für Polymerforschung, Germany and Stanford Univ., Germany; *D. Kambhampati, T. Liebermann, T. Neumann,* Max-Planck-Institut für Polymerforschung, Germany

Surface plasmon spectroscopy (SPS) is widely used as a surface-sensitive technique to characterize thin film architectures, or to monitor kinetic processes like biorecognition and binding events or photo-reactions in these layers. We describe an extension of the method combining the field-enhancements obtainable at the resonant excitation of surface plasmons with fluorescence detection schemes. Controlling the balance between the evanescent character of the surface mode and the energy (Förster) transfer between the chromophores and (the acceptor states of) the metal substrate sensitivity enhancements of more than 2 orders of magnitude compared to SPS can be achieved (though not label-free). We demonstrate the potential of this mode of operation for the quantitative evaluation of hybridization reactions between surface-immobilized probe oligonucleotides (15-mers) and complements from solution. It is shown that a simple Langmuir adsorption/desorption model describes the experimental results. Single base mismatches can account for a decrease in the equilibrium constant by two orders of magnitude, a second mismatch can give a reduction by another 3 orders. A further extension that will be introduced is the simultaneous observation of several hybridization/dehybridization reactions on a 3 x 3 matrix of 9 different sensor spots by fluorescence microscopy.

3:00pm **BI-TuA4 Characterization of Supported Biomimetic Films Using Broadband Vibrationally Resonant Sum-Frequency Generation**, ***K.A. Briggman,*** *T. Petralli-Mallow, L.J. Richter, A.L. Plant, J.C. Stephenson,* National Institute of Standards and Technology

Supported organic films have received considerable attention as model biological membranes, as well as biomolecular templates for the development of biomimetic devices. A complete characterization of these biomimetic films requires the application of in-situ techniques, capable of probing fully hydrated systems. We have been exploring the potential of broadband vibrationally resonant sum frequency generation (SFG) as an in-situ probe for the study of hybrid bilayer membranes (HBMs). Our novel broadband approach@footnote 1@ provides a complete SFG spectrum over a window of several hundred wavenumbers, combining interface sensitivity and molecular specificity with the advantages of short acquisition times and no need for wavelength tuning. We have acquired vibrational SFG spectra of a variety of supported biomolecular compounds, including phospholipids in HBMs. A discussion of the preparation and stability of the HBMs as examined by SFG will be presented. @FootnoteText@ @footnote 1@Vibrationally resolved sum-frequency generation with broad-bandwidth infrared pulses, Opt. Lett. 23 1594 (1998).

3:20pm **BI-TuA5 Biosensors in Biomaterials Research**, ***K.I. Lundström,*** Linköpings Universitet, Sweden **INVITED**

There are several surface physical tools, which are used to study the interaction between biomaterials and tissue. Many of them require special sample preparation and can not be used to follow the kinetics of interaction at the biomaterial surface. They can thus not be considered for in vivo applications either. Biosensor technologies developed for the monitoring of biomolecular interactions and utilizing (surface) physical phenomena as the detection principle should, however, be suitable for kinetic studies both in vivo ant in vitro. In this contribution some of the biosensing technologies for biomolecular interactions with and at surfaces are described, with special attention to surface plasmon resonance instrumentation and quartz crystal microbalances. It is concluded that by modifying the surface of such biosensors it is possible to study several important phenomena related to biomaterials and biocompability. Furthermore it is concluded that biosensors can be used also to monitor parameters outside the biomaterial itself, such as coagulation factors, inflammatory mediators etc. Biosensors for in vivo studies of biomaterials are also touched upon. The present use of biosensors for biomaterials related research is reviewed. A few examples from studies of e.g. plasminogen bleeding surfaces, complement activation and blood coagulation at surfaces are given. Finally some future possibilities of surface oriented biosensors for biomaterial research are speculated upon. This includes for the elucidation of the behavior of (single) cells adsorbed on or interacting with biomaterial surfaces.

4:00pm **BI-TuA7 Direct Probing of the Surface Ultrastructure and Molecular Interactions of Living Microbial Cells with Atomic Force Microscopy**, ***Y.F. Dufrene,*** *C.J.P. Boonaert, P.G. Rouxhet,* Universite Catholique de Louvain, Belgium

Understanding biointerfacial phenomena such as cell aggregation and cell adhesion requires knowledge of the surface structure and physico-chemical properties of living cells with a nanometer scale resolution. In this work, atomic force microscopy (AFM) was used to determine, in physiological conditions, the ultrastructure and molecular interactions at the surface of living spores of Phanerochaete chrysosporium and their changes during germination. Cell immobilization was achieved by mechanical trapping in porous membranes. High-resolution images recorded on dormant spores showed that the surface was uniformly covered with a regular pattern of rodlets. These structures were several hundreds nm in length and had a periodicity of about 10 nm, in excellent agreement with freeze-etching characterization. Force-distance curves recorded between a silicon nitride probe and the spore surface showed no adhesion forces upon retraction. Dramatic changes of cell surface ultrastructure and molecular interactions occurred during germination. Germinating spores had a very smooth surface, partially covered with granular structures which were the residues of the rodlet layer. Force-distance curves recorded on smooth areas showed strong adhesion forces. These are attributed to binding of polysaccharides, which have been detected by X-ray photoelectron spectroscopy (XPS) and considered to be responsible for spore aggregation. The approach presented here offers new possibilities for probing the local surface properties of prokaryotic, animal and plant cells in the native state.

4:20pm **BI-TuA8 Contact Mechanical Properties of Confined NIPAM Films at the Biomaterial Interfaces***, **R. Luginbuehl**, M.D. Garrison, Y.V. Pan, R.M. Overney, B.D. Ratner,* University of Washington

Smart polymeric materials, which change their structural properties upon stimulation, are of highest interest for industrial applications in surface coating and printing, sensor technology, biotechnology, medicine, and biomaterial research. Progress in precision engineered surfaces for biosensor applications strongly depend on appropriate techniques to analyze surfaces at the micro and nanometer level. Recently, considerable research effort has focused on the investigation of co-polymers and grafted polymers containing N-isopropylacrylamide (NIPAM). These polymers can be engineered to undergo thermally induced structural and mechanical phase transitions around 32 ÂºC, which is drawn by hydrophobic forces and hydrogen bonding. The structural phase transition is accompanied by a change in volume, and therefore a change in mechanical properties, as well as a change in the surface free energy. We carried out scanning force microscope (SFM) investigations on surface confined NIPAM films. Thin films (thickness < 10 nm) were obtained by polymerization on selected substrates. Novel SFM techniques permit the observation of the transition behavior at the nanometer scale. Photolithographically patterned thin films were used to isolate changes in the polymer structure relative to a reference substrate. Contact mechanical properties, volume transition, and the interfacial energy were monitored as a function of the system temperature. The introduced SFM technique offers a unique combination of microscopy with spectroscopic analysis of surface interactions and local subsurface structural properties.

4:40pm **BI-TuA9 Novel Biomaterials through Tailoring of Solid Surfaces***, **J. Rühe**,* Max-Planck-Institute for Polymer Research, Germany

The modification of materials by monolayers of polymers, which are covalently attached to the surface of the substrate, is a very attractive way to improve the properties of solids in bio-oriented applications. We describe several new pathways for the synthesis of surface-attached ultrathin polymer films, which carry functional groups relevant for biological or biomedical applications. The polymer molecules are either grown at the surface of the substrate in situ by using self-assembled monolayers of initiators or preformed polymers are (photo-)chemically attached to the material, which is to be modified. Additionally, the formation of ultrathin, patterned networks of functional polymers will be described. Examples for groups contained in the monolayers are peptide moieties, which could act as cell recognition sites and DNA fragments for biochip applications. The characterization of the monolayers, especially the swelling of the layers in an aqueous environment, will be described.

5:00pm **BI-TuA10 Photoisomerization and Photo-induced Alignment of Ordered Polymer Ultrathin Films Containing DNA and Polypeptide Layers: Possibilities for Optobioelectronic Substrates***, **R.C. Advincula**,* University of Alabama at Birmingham, US*; Y. Wang, E. Fells, E. Wallace,* University of Alabama at Birmingham

Alternate polyelectrolyte deposition (APD) is a relatively new technique for fabricating multilayer ultrathin polymer films. Since the polymers are adsorbed from solution, it opens up the possibility for incorporating biological macromolecules such as proteins, or nucleic acids in the active site that may be interesting for biosensing or biocompatibility issues. In the case of DNA molecules, selectivity arises from the interaction with various specific DNA reagents such as intercalators and DNA-complementary (hybridization) interactions. The multilayer complex films are also good model systems to investigate interaction between polynucleotides and polypeptides. The advantage of ultrathin film geometries in substrate supported systems is that they allow direct structural analysis using X-ray, FT-IR, SPS, etc. on a number of substrates, e.g. ITO-, Gold- coated glass, Si, etc. In this work, we report the formation of highly ordered ultrathin films containing DNA and/ or Polylysine/ Azobenzene dye multilayers fabricated using the alternate polyelectrolyte deposition (APD) approach. An important modification is the incorporation of photoisomerizable azobenzene dyes in the films to explore the possibility of using these films for some optobioelectronic applications. The photoisomerization of the dyes were investigated with respect to thickness, irradiation parameters, pair combinations, etc. The formation of polypeptide-dye multilayer complexes resulted in photo-induced circular and linear dichroism. This was investigated using polarized UV-vis spectroscopy, ATR, and SPS configurations. The conformation of the polypeptide and the DNA was investigated by FT-IR. In-situ adsorption experiments were investigated using ellipsometry and QCM.

Electronic Materials and Processing Division
Room 608 - Session EM-TuA

High Dielectric Constant Materials and Thin Oxides

Moderators: Y.J. Chabal, Bell Laboratories, Lucent Technologies, K.T. Queeney, Bell Laboratories, Lucent Technologies

2:00pm **EM-TuA1 Challenges in Gate Dielectric Scaling***, **D.P. Monroe**, B.E. Weir, M.A. Alam, J. Bude, P.J Silverman, T. Sorsch, M.L. Green, A. Ghetti, Y. Ma, Y. Chen, F. Li,* Bell Labs, Lucent Technologies **INVITED**

Extrapolation of current trends in CMOS suggest that the gate dielectric of 2010 will have a capacitance equivalent to <15Å of SiO@sub 2@, including the nonzero thickness of the charge sheets in gate and substrate. It must withstand penetration of elements such as Boron during processing, and of electrons and holes during operation. It must tolerate damage from highly energetic carriers excited by the voltages on gate and drain over a multi-year operating life. Proposed replacements for SiO@sub 2@ must also demonstrate materials compatibility with the Si substrate and the gate material (currently also Si). The successful candidate will have a fewer than one interface defect for 10,000 atoms, and a uniformity across wafers, lots, and runs of better than 10% (3@sigma@). We will discuss these daunting materials and processing challenges from a transistor and circuit perspective, concentrating on the capacitance, mobility, boron penetration, and time-dependent dielectric breakdown of SiO@sub 2@ and nitrided oxides thinner than 30Å, as measured by ellipsometry. The electrical thickness of such oxides is thicker by at least 5Å, depending strongly but reproducibly on the oxide field. Simple measurements of this dependence are critical to understanding the transistor drive capability and the leakage current. The breakdown properties are more strongly governed by the applied potentials than the field. However they are strongly sensitive to the polarity of the gate voltage, even after care has been taken to include the large effects of band bending. This indicates the important role of the carrier dynamics in the anode. The "soft" breakdown of these thin oxides indicates a reduced role of positive feedback that results in higly conductive filaments in thicker oxides; indeed, some transistors continue to function even after "breakdown." We will outline some ideas for the physical mechanisms underlying the special properties of breakdown in these films.

2:40pm **EM-TuA3 Investigation of Titanium Nitride Gates for Tantalum Pentoxide and Titanium Dioxide Dielectrics***, **D.C. Gilmer**, C.C. Hobbs, L. La, B. Adetutu, J. Conner, M. Tiner, L. Prabhu, S. Bagchi, P. Tobin,* Motorola

The continuing push to decrease the feature size of microelectronic devices is hampered by some of the physical properties of the current materials. According to the National Technology Roadmap for Semiconductors (NTRS) projections, deep sub-micron device scaling indicates that silicon dioxide gate dielectrics must be scaled to less than 25 angstroms. It is generally accepted however, that such scaling will not be practical due to the rapid increase in tunneling current and resultant decrease in lifetime for these very thin silicon dioxide gate dielectrics. One alternative is to replace silicon dioxide with a material having a higher dielectric constant that will allow the use of thicker, less leaky, films. Towards this end, compounds such as tantalum pentoxide and titanium dioxide have been evaluated to replace silicon dioxide as a gate dielectric. Poly-silicon, currently used as the gate metal in MOSFETs, has been shown to react with transition metal oxides such as tantalum pentoxide and titanium dioxide to form an undesirable interfacial layer between the poly-silicon and metal oxide. Due to this incompatibility of poly-silicon metal gates with tantalum pentoxide or titanium dioxide gate dielectrics, an alternate metal gate material will need to be adopted for these alternative gate dielectrics. Titanium nitride (TiN), a mid-gap metal, has been extensively studied (and used) as a barrier material in many microelectronic devices. This paper reports on the investigation of physical vapor deposited and chemical vapor deposited titanium nitride for the application of a gate metal in capacitors (with sidewall spacers) using tantalum pentoxide or titanium dioxide as the gate dielectric. Electrical characteristics from C-V and I-V data, along with high resolution transmission electron microscopy of the TiN/gate oxide interface, for as-deposited and thermally annealed samples will be reported.

3:00pm **EM-TuA4 Separate and Independent Reductions in Direct Tunneling in Oxide/Nitride Stacks with Monolayer Interface Nitridation Associated with the i) Interface Nitridation and ii) Increased Physical Thickness***, Y. Wu, H. Niimi, H. Yang, G. Lucovsky,* North Carolina State University

Reduction of direct tunneling in aggressively-scaled CMOS devices with deposited oxide/nitride stacks and/or oxynitride alloys is crucial for replacement of thermally-grown oxides. We have identified two separate and independent mechanisms for tunnel current reduction that have been combined in oxide/nitride stacks with monolayer interface nitridation to yield current densities <10@super -2@ A/cm@super 2@ for stacks with oxide-equivalent thickness <1.6 nm. Fabrication of these stacks combines remote plasma-assisted nitridation and deposition processes to independently control nitrogen concentration profiles at the atomic layer level at interfaces and in bulk films. The order of interface nitridation is crucial and monolayer concentrations to reduce direct tunneling by ~ten require two 300°C steps: i) first, remote plasma-assisted oxidation of H-terminated Si(100) to form a ~0.6 nm passivating oxide, followed by ii) remote plasma-assisted nitridation to insert a monolayer of N-atoms at the Si-interface. XPS results indicate that the reduction in tunneling derives from differences in interfacial suboxide bonding associated with nitridation. Since tunneling increases exponentially with decreasing film thickness, incorporation of nitride layers in O/N stacks allows use of physically thicker films while maintaining capacitance equivalent to thinner oxides. We find that increases in thickness are in part mitigated by decreases in the product of the tunneling mass and thickness-averaged-barrier-height in the nitrides, limiting tunneling decreases to ~10-20 with respect to single layer oxides. However, using remote plasma-assisted processing to separately control interfacial and bulk dielectric nitrogen profiles, it has been possible to combine these two order of magnitude decreases and achieve reductions in tunneling of more than 200 in N/O/N stacks. These have been included in NMOS- and PMOSFETs which display excellent current drive and high reliability.

3:20pm **EM-TuA5 High K Gate Dielectrics for Sub-100nm CMOS***, D.L. Kwong,* University of Texas, Austin **INVITED**

With the scaling down of device dimensions, conventional SiO2 and oxynitride films will reach their physical limits in terms of thinning. As a result, there has been a great interest in the development of high permittivity materials as MOS gate dielectrics for sub-100nm CMOS. In this talk, the requirements and significant challenges in developing high K gate dielectrics with performance and reliability specs consistent with NTRS roadmap are reviewed. Results will be presented to demonstrate the importance of the interface layer at highK/Si interface. The choice of high K materials and issues associated with process integration for sub-100nm CMOS will also be discussed.

4:00pm **EM-TuA7 Evidence of Aluminum Silicate Formation at the Al@sub2@O@sub3@/Si Interface for Thermal and Plasma Enhanced Chemical Vapor Deposited Al@sub2@O@sub3@ Thin Films***, D. Niu, T.M. Klein, G.N. Parsons,* North Carolina State University

An important issue in the determination of a suitable high k gate dielectric for advanced CMOS device is the stability of the material with the Si substrate. An insulator with a covalent nature, a limited number of oxidation states and a resistance to ionic transport would be an attractive candidate for this application. This paper investigates the properties of thin Al@sub2@O@sub3@ films as a possible higher-k (12~15) alternative to SiO@sub2@. The films were formed in a 6" compatible triode plasma reactor which was also used for thermal CVD. A variety of aluminum precursors were studied, including Al acetylacetonate, Al sec-butoxide, and Al isopropoxide. A new liquid precursor, triethyl-dialuminum tri-sec-butoxide was also tested. The new precursor is safe, easy to handle and does not decompose with prolonged heating at 150°C. O@sub2@, N@sub2@O and H@sub2@O were used as oxygen sources in both plasma and low temperature (300-400°C) thermal deposition. In the thermal process, H@sub2@O resulted in deposition rates >10 Å/sec, with Ea=0.16 eV, compared to 0.1 Å/sec and Ea=1.1 eV for O@sub2@ precursor. IV, CV, TEM, ellipsometry and nuclear reaction profiling were used to characterize thin (20-300 Å) Al@sub2@O@sub3@ films on silicon. The films show acceptably low leakage current, 3X10@super-5@ A/cm@super2@ at 1 V for a 5 nm thick film. In some process conditions, clear evidence for mixing of aluminum oxide and silicon is observed in the capacitance measurement, consistent with the optical and structural evaluations. A fit of the capacitance data to a simple model is used to predict the dielectric constant of aluminum silicate layer.

4:20pm **EM-TuA8 Thermally Grown Gate Insulators for Heterostructure p-MOSFETs***, D.W. Greve, A.C. Mocuta,* Carnegie Mellon University

With decreasing channel length and increasing channel electric field, it is increasingly difficult to maintain adequate transistor ON currents in scaled MOS technologies. Germanium-silicon heterostructure p-MOSFETs potentially offer improvements in channel mobility of 30-50%; however, devices with thick channels and high germanium fraction may relax during thermal oxidation or other subsequent high-temperature processing. We have fabricated heterostructure MOSFETs and MOS capacitors using germanium-silicon-carbon epitaxial layers grown by UHV/CVD. We will show that low-carbon Si@sub 1-x-y@Ge@sub x@C@sub y@ channels do not relax for thermal anneals as high as 900 C. Consequently it is possible to use a thermally grown gate SiO@sub 2@ gate insulator while still maintaining a high channel charge capacity in the Si@sub 1-x-y@Ge@sub x@C@sub y@ layer. This has been demonstrated using heterostructure MOS capacitors with 30 nm Si@sub 1-x-0.002@Ge@sub x@C@sub 0.002@channels in which the germanium fraction x has been linearly graded from x=10% to x=40%. For cap layers approximately 6 nm in thickness after gate insulator growth, germanium surface segregation during epitaxial layer growth leads to a poor quality insulator-semiconductor interface. However, for thicker cap layers nearly ideal MOS C(V) characteristics are observed. We will also report on heterostructure p-MOSFETs which have been fabricated with Si@sub 1-x-y@Ge@sub x@C@sub y@ channels and thermally grown gate insulators. It will be shown that these devices exhibit channel mobilities of 200 cm@sup 2@/Vsec at room temperature, which is comparable to that reported with Si@sub 1-x@Ge@sub x@ channels and plasma silicon dioxide gate insulators. This demonstration opens the way toward the application of heterostructure p-MOSFETs in practical CMOS technologies.

4:40pm **EM-TuA9 Deposition of ZrO@sub 2@/SiO@sub 2@ Alloys by 300° Remote Plasma Processing for Alternative High-K Gate Dielectrics in Aggressively Scaled CMOS Devices***, R. Therrien, B. Raynor, D. Wolfe, G. Lucovsky,* North Carolina State University

Stimulated by targeted performance goals for aggressively-scaled CMOS devices, there has been much interest in alternative gate dielectric materials to replace SiO@sub 2@. The choice of materials is based on identifying insulating oxides with dielectric constants greater than SiO@sub 2@, so that physically-thicker films, anticipated to have reduced direct tunneling, will be equivalent to thinner oxides. This paper describes the deposition of ZrO@sub 2@/ SiO@sub 2@ alloy films by 300°C remote plasma-assisted CVD. This approach has two potential advantages with respect to conventional thermal CVD. First, by injecting the Zr precursor, Zr(IV) t-butoxide, and the Si precursor, silane, downstream from the plasma region, and driving the CVD reaction with active O-species extracted from an upstream O@sub 2@/He plasma, complete oxidation of Zr and Si has been confirmed by on-line AES and off-line FTIR. Films prepared in this way are amorphous as-deposited, as determined from FTIR and electron diffraction, and more importantly remain amorphous up to at least 900°C after annealing in an inert ambient. This paper describes the deposition process, and identifies the way in which the relative concentration of ZrO@sub 2@ to SiO@sub 2@ has been controlled to achieve deposition of films approaching the compound ZrSiO@sub 4@ composition. Other properties of these films relative to their role as a replacement dielectrics are discussed; e.g., optical studies of the band-gap, and electrical capacitance-voltage and current-voltage characteristics are presented. These allow us to obtain i) the static dielectric constant, ii) the conduction band offset energy with respect to Si and iii) the tunneling electron mass. Based on these measurements, ZrO@sub 2@/SiO@sub 2@ alloys in conjunction with hyper-thin (~0.5 nm), nitrided SiO@sub 2@ interfacial layers can be used to scale the oxide-equivalent dielectric thickness down to about 1 nm.

Flat Panel Displays Topical Conference
Room 604 - Session FP+OE+EM-TuA

Thin Film Transistor Materials and Devices

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

2:00pm **FP+OE+EM-TuA1 Nanoprobing Electrical Transport in Organic Semiconductors***, C.D. Frisbie,* University of Minnesota **INVITED**

Commercial interest in mechanically flexible plastic electronics is the key motivator behind efforts to fabricate transistors, light-emitting diodes, and lasers from organic thin films. Continued development depends on increasing comprehension of factors affecting charge carrier mobility. In particular, the importance of film microstructure on transport in organic films has been recognized, but is currently not well understood. In this talk, I will describe experiments designed to address microstructural effects on conductivity in polycrystalline organic films. Our approach is to probe transport in individual grains, or even small collections of grains, which we characterize by atomic force microscopy (AFM). Experiments have focussed on crystalline grains of the molecular semiconductor sexithiophene (6T). Isolated grains of 6T are grown by vacuum sublimation onto SiO2/Si substrates. The crystals range from 1-6 molecular layers (2-14 nm) in thickness with diameters on the order of a micron. In one approach, these thin crystals are contacted with source and drain electrodes fabricated by electron-beam lithography; heavily doped Si underneath the SiO2 serves as a gate electrode. The resulting transistor structures are used to probe field effect conductance and carrier mobility as a function of temperature (5-300K) and the number of discrete molecular layers in the crystals. The second experiment uses a conducting AFM probe as a positionable electrical contact to grains contacted by a fixed electrode at the other end. This configuration allows variation of the tip-electrode separation, yielding the single grain resistivity and an estimation of the organic-metal contact resistance. Resistances associated with defects, e.g., a single grain boundary between adjacent crystals, may also be measured. In both types of experiments, the conjunction of AFM imaging with transport measurements is critical to correlating transport properties with specific microstructures.

2:40pm **FP+OE+EM-TuA3 Photolithographically Defined Pentacene Thin Film Transistors on Flexible Plastic Substrates***, **D.J. Gundlach**, C.D. Sheraw, H. Klauk, J.A. Nichols, J-R. Huang, T.N. Jackson,* The Pennsylvania State University

We report photolithographically-defined pentacene thin film transistors (TFTs) on flexible plastic substrates with performance similar to hydrogenated amorphous silicon (a-Si:H) devices. Organic TFTs fabricated on flexible plastic substrates are of interest for mechanically rugged, low-cost broad-area electronic applications. Pentacene TFTs with performance similar to a-Si:H TFTs have been reported,@footnote 1@ however, such devices are typically fabricated on oxidized silicon or glass substrates. Since photolithographic processing of organic semiconducting materials is problematic, such devices, including more recent devices on polymeric substrates,@footnote 2@ typically use source and drain contacts deposited through a shadow-mask after the organic active layer deposition. We have fabricated photolithographically-defined pentacene TFTs on polyethylene naphthalate (PEN) and polyimide (PI) films. For ease of processing, the films were mounted to silicon wafers using a pressure sensitive silicone adhesive and pre-shrunk by heating to 150°C for 1 hour in vacuum. A 30 nm thick Ni gate electrode, 160 nm thick SiO@sub 2@ gate dielectric, and 80 nm thick Pd source/drain contacts were deposited by ion-beam sputter deposition. The TFTs were completed by thermally evaporating pentacene onto substrates heated to 60°C. All deposited layers were photolithographically-defined using a two-layer resist lift-off process. Field-effect mobility larger than 0.3 cm@super 2@/V-s was extracted for TFTs on both PI and PEN film, current on/off ratio was greater than 10@super 5@, and subthreshold slope was less than 1.5 V/decade, all obtained using drain-to-source and gate-to-source biases of -30 volts or less. @FootnoteText@ @footnote 1@ Y-Y. Lin, D. J. Gundlach, S. F. Nelson, and T. N. Jackson, IEEE Electron Device Lett., vol. 18, pp. 606-608, 1997. @footnote 2@ C. D. Dimitrakopoulos, S. Purushothaman, J. Kymissis, A. Callegari, and J. M. Shaw, Science, vol. 283, pp. 822-824, 1999.

3:00pm **FP+OE+EM-TuA4 Reduced Process Complexity Organic Thin Film Transistors***, **H. Klauk**, D.J. Gundlach, M. Bonse, T.N. Jackson,* The Pennsylvania State University

The performance of organic thin film transistors (TFTs) has improved dramatically over the past few years and recently, pentacene TFTs with carrier mobility of 0.6 cm@super 2@/V-s were demonstrated on glass substrates.@footnote 1@ The TFT device structure used in this earlier work required 4 material depositions and 4 lithography steps: one each for the gate, the gate dielectric, the source/drain contacts, and the pentacene active layer. Patterning of the pentacene layer is important to avoid leakage since pentacene TFTs often have large positive threshold voltage. We report here a simplified device structure for depletion-mode pentacene TFTs. Only 3 material depositions and 3 lithography steps are required and the same metal deposition is used for the gate electrode and the source/drain contacts. Gate-to-source and gate-to-drain overlap are not required, since the pentacene layer is normally conducting, thus allowing a drain current to flow at zero gate bias; devices are turned off by applying a positive gate bias. Palladium was used for the gate and source/drain metal, and low-temperature (80°C) ion-beam sputtered SiO@sub 2@ was used as the gate dielectric; both layers were patterned by lift-off. To pattern the pentacene active layer, a double-layer photoresist technique was used to create a reentrant profile over which the pentacene was deposited by evaporation. Upon deposition, the pentacene layer breaks over the resist profile, leaving isolated TFT areas. At a relatively low drain-source voltage of -20 V, devices have carrier mobility as large as 0.3 cm@super 2@/V-s, on/off current ratio near 10@super 5@, subthreshold slope as low as 0.9 V/decade, and threshold voltage between +10 V and +17 V. @FootnoteText@ @footnote 1@ Hagen Klauk, David J. Gundlach, Jonathan A. Nichols, and Thomas N. Jackson, "Pentacene Organic Thin-Film Transistors for Circuit and Display Applications," IEEE Transactions on Electron Devices, vol. 46, no. 6, June 1999.

3:20pm **FP+OE+EM-TuA5 Soft Lithographic Patterning and Low Temperature Film Deposition: Methods to Fabricate Amorphous Silicon Thin Film Transistors at Low Temperature***, **H.-C. Jin**, J.R. Abelson, M.K. Erhardt, R.G. Nuzzo,* University of Illinois, Urbana

We fabricate amorphous silicon thin film transistors on glass substrates at low temperature (125@super o@C) using "soft" lithographic patterning in place of traditional photolithography. In soft lithography, polymer templates are formed on the film by holding an elastomer block containing the desired pattern in contact with the substrate, flowing an uncured precursor into the micro-channels of the pattern, then curing the polymer. Such templates replace photoresist for all etch and deposition steps, and have been successfully used for the fabrication of multilayer device architectures with micron-scale feature resolution. It appears possible to pattern sub-micron features, as well as large area and curved substrates. In this talk, we show the patterning methodology, preliminary results for TFT devices on planar and curved substrates, and discuss future prospects.

3:40pm **FP+OE+EM-TuA6 Low Damage Etching Utilizing Activated Hydrogen Beam for ITO Transparent Electrode in Flat Panel Display***, **T. Miyata**, T. Minami, M. Ishii,* Kanazawa Institute of Technology, Japan

Recently, low damage dry etching has become necessary for transparent electrode patterning in flat panel display fabrication. This paper introduces a newly developed low damage and high rate etching technique utilizing an activated hydrogen beam to etch Sn-doped indium oxide (ITO) transparent conducting films. The etching was carried out using an apparatus consisting of an etching chamber and an activating chamber interconnected with a 0.9 mm-diameter orifice; the pressure in the activating chamber was higher than that in the etching chamber. The hydrogen gas introduced into the activating chamber was first activated by applying microwave power and then introduced through the orifice into the etching chamber. The etching was accomplished by the activated hydrogen beam acting on patterned photoresist coated ITO films placed on a sample holder. The etching rate was strongly dependent on conditions such as sample temperature, orifice-sample separation and pressure in the etching chamber. It should be noted that the ITO film was only etched at sample temperatures above 160@super o@C and the etching rate increased as the sample temperature was increased. A maximum etching rate above 50 nm/min was obtained at a sample temperature of 220@super o@C. These results suggest that ITO films are mainly etched by chemical reactions.

4:20pm **FP+OE+EM-TuA8 Excimer Laser Processing for a-Si and poly-Si Thin Film Transistors for Imager Applications***, **J.P. Lu**, P. Mei, R.T. Fulks, J. Rahn, J. Ho, Y. Wang, J.B. Boyce, R.A. Street,* Xerox Palo Alto Research Center **INVITED**

Pulsed Excimer-Laser Annealing (ELA) has become an important technology to produce high performance Thin Film Transistors (TFTs) for large area electronics. The application of these advanced TFTs in flat pannel displays@footnote 1@ and flat panel imagers for two-dimensional X-ray imaging have attracted much interest. TFTs made from laser crystallized poly-Si thin films with mobility higher than 100 cm@super 2@/Vs can be consistently achieved and are well suited for the integrated driver circuits. Recently, leakage currents as low as 2fA/µm at 5V for these poly-Si TFTs have been achieved and enable one to consider making flat panel imagers using a full poly-Si process. Laser doping@footnote 2@ or dopant activation is another important application of the ELA process. Using a laser doping process, we have fabricated a-Si TFTs with self-aligned poly-Si source/drain contacts. These new devices have reduced source/drain parasitic capacitance and their channel length can be easily scaled down without stringent lithography requirements. Excellent DC performance, such as low leakage current (0.02fA/µm), sharp turn on (0.44V/decade) and high mobility of a-Si TFTs are preserved. In addition, good AC performance of these self-aligned a-Si TFTs has been demonstrated in four phase dynamic shift registers operating at 250kHz. In this talk, these two areas will be reviewed along with a report on the current status in developing poly-Si TFTs and self-aligned a-Si TFTs using ELA process for flat panel imager applications. @FootnoteText@ @footnote 1@ J. G. Blake, M. C. King, J. D. Stevens III, and R. Young, Solid State Technology, p151, May 1997. @footnote 2@ P. Mei, G. B. Anderson, J. B. Boyce, D. K. Fork, and R. Lujan, Thin Film Transistor Technologies III, Electrochemical Soc. Proc., PV 96-23, p51 (1997).

5:00pm **FP+OE+EM-TuA10 Solid-phase Crystallization of Hydrogenated Amorphous Silicon-Germanium Alloy Films***, **O.H. Roh**, I.H. Yun, J.-K. Lee,* Chonbuk National University, Korea

We have investigated the solid-phase crystallization of hydrogenated amorphous silicon-germanium alloy (a-Si@sub 1-x@Ge@sub x@:H) films by using electron spin resonance (ESR) and x-ray diffraction measurements. The films were deposited on Corning 1737 glass in a plasma-enhanced chemical vapor deposition system using SiH@sub 4@ and GeH@sub 4@ gases. The substrate temperature was 200°C and the r.f. power was 3W. The films were then annealed to be crystallized at 600°C in a N@sub 2@ atmosphere. The total spin density first increased with annealing time due to hydrogen evolution, and then rapidly decreased as the film was crystallized. The Ge dangling bond spin density increased faster with annealing time than the Si dangling bond spin density. However, it was observed that the H evolution from Si-H bond and Ge-H bond was strongly affected by the Ge composition of the films.

Magnetic Interfaces and Nanostructures Technical Group Room 618/619 - Session MI-TuA

Magnetic Spectroscopies

Moderator: S.D. Bader, Argonne National Laboratory

2:00pm **MI-TuA1 Electronic Structure of Single Crystal CrO@sub 2@***, **C.B. Stagarescu**, X. Su, D.E. Eastman,* University of Chicago*; K.N. Altmann, F.J. Himpsel,* University of Wisconsin, Madison*; A. Gupta,* IBM T.J. Watson Research Center

CrO@sub 2@ was predicted to exhibit half-metallic behavior with 100% spin polarization for electrons at the Fermi level, making it an ideal spin-injector for spin-polarized tunnelling junctions. Recently, a spin polarization of 90% at the Fermi level has been measured with a superconducting point contact.@footnote 1@ We have determined the relevant electronic states using polarization-dependent X-ray absorption (XAS) from the Cr 2p and O 1s core levels into the Cr 3d and O 2p states near the Fermi level, by X-ray magnetic dichroism (XMCD) at these edges, and by spin-polarized photoemission measurements. A clear picture emerges from the O 1s absorption edge, where a sharp peak is observed at 529.2 eV, followed by two peaks at energies of 2.1 and 3.5 eV higher. The first peak is excited only by the electric field vector (E) in the a-b plane, implying O 2p orbitals lying in that plane. It also exhibits a positive XMCD signal, which demonstrates significant hybridization of these (O 2p@sub x@, 2p@sub y@) states with the magnetic Cr 3d states of t@sub 2g@ character that produce the expected 100% majority spin polarization at the Fermi level. The two upper peaks have the opposite polarization dependence, implying an orientation of their O 2p orbitals mainly along the c axis (2X increase in magnitude from E parallel to the a axis to E perpendicular to the a axis, compared to a 10X decrease for the first peak). XMCD spectra obtained with magnetization along the easy (c) and hard (a) axis are compared. The consequences of these results for current models of the electronic structure are discussed. @FootnoteText@ @footnote 1@ R. J. Soulen et al, Science, 282, 85 (1998).

2:20pm **MI-TuA2 Underlying Simplicity of Magnetic Dichroism in the Photoelectron Spectroscopy of Gd***, **J.G. Tobin**, S.R. Mishra,* Lawrence Livermore National Laboratory*; T.R. Cummins, G.D. Waddill,* University of Missouri, Rolla*; G. van der Laan,* Daresbury Laboratory, UK

Despite severe complexity in the 'raw' spectra of the Gd 5p's, the linear dichroic differences from remanently magnetized Gd/Y exhibit a startling underlying simplicity and consistency. The Gd 5p peaks display a strong cross sectional increase due to 'resonant photoemission' in the photon energy range of 135 to 150 eV. To properly model the pairs of 'raw' spectra acquired in linear dichroism experiments, an atomic model including multielectronic effects such as orbital momentum coupling is required. [1] However, the difference spectra obtained from the pairs are remarkably simple and consistent, in both experiment and atomic simulations. The development of a simplified one-electron picture to analyze the dichroic differences will also be discussed. S.R. Mishra, T.R. Cummins, G. D. Waddill, W.J. Gammon, G. van der Laan, K.W. Goodman, and J.G. Tobin, 'On the Nature of Resonant Photoemission in Gd,' Phys. Rev. Lett., 81, 1306 (1998).

2:40pm **MI-TuA3 Element-Resolved Magnetism Using Core-Resonant Magneto-Optical Techniques***, **J.B. Kortright**, S.-K. Kim,* Lawrence Berkeley National Laboratory **INVITED**

Most magnetic films of current interest involve multiple magnetic species either homogeneously or heterogeneously distributed in single or multiple layers; examples include alloy or compound thin films, exchange-coupled layers or phases, and interfacial magnetism. A variety of soft x-ray magneto-optical techniques can resolve the aggregate magnetic response of such materials into that of the individual magnetic constituents, thereby offering opportunities to obtain a more detailed microscopic understanding of the macroscopic properties of interest. We have been extending traditional photon-based magneto-optical techniques, embodied in the complex Faraday and Kerr effects, from the near-visible regions into the soft x-ray range containing core levels of the 3d transition metals with associated large resonances in magneto-optical properties. Measuring the polarization of transmitted and reflected beams, in addition to their intensity, provides information that can, e.g., determine elemental moments both longitudinal and transverse to the propagation direction. In addition to field-dependent element-resolved information (hysteresis loops), spatial information both laterally and in depth on the nanometer scale and up is available from scattering and microscopy. Examples of the application of these techniques to better understand questions in exchange-coupled layers and alloy films will be given. @FootnoteText@ This work was supported by the Director, Office of Energy Research, Office of Science, Materials Sciences Division, of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

3:20pm **MI-TuA5 Interatomic Effects in Resonant Photoemission in Fe/Cr Alloys and Bilayers***, **E. Arenholz**,* Lawrence Berkeley National Laboratory*; A.W. Kay, C.S. Fadley,* Lawrence Berkeley National Laboratory and Univ. of California, Davis

Recently, first measurements and theoretical calculations of an interatomic multi-atom resonant photoemission effect (MARPE) have been reported by our group in measurements on several magnetic metal oxides (Science 281, 679 (1998)). MARPE occurs when the photon energy is tuned to a core-level absorption edge of an atom neighboring the emitting atom, with the photoemitting level having a lower binding energy than the resonant level; the resonant excitation is then found to significantly increase the photoemission intensity. We have now observed such effects in Fe/Cr alloys and bilayers. E.g. in Fe@sub 0.5@Cr@sub 0.5@, the Cr 2p intensity is enhanced by 20% when the photon energy is tuned to the Fe L@sub 3@ edge. Since MARPE is an interatomic effect the resonant enhancement of the Cr intensity in Fe/Cr alloys is expected to scale linearly with the number of Fe near neighbors. Although a monotonic decrease in the MARPE effect in Cr with decreasing Fe concentration is indeed found, deviations from the linear relationship expected from random mixing of Fe and Cr are observed. These findings will be discussed in terms of possible compositional clustering in Fe/Cr alloys, including additional data from Fe/Cr bilayers that were used to estimate the sensing length of the MARPE effect in this system. First observations of magnetic circular dichroism in the effect will also be presented.

3:40pm **MI-TuA6 Dispersions of Metallic Quantum Well States in the Cu/fccM(100) [M = Ni, Co, Fe] Systems***, **A.G. Danese**, R.A. Bartynski,* Rutgers University

The study of the electronic properties of nonmagnetic/ferromagnetic bi-layers is essential to understanding the phenomenon of oscillatory magnetic coupling that is seen in magnetic multilayers. Using a phase accumulation model, we have calculated the dispersions of metallic quantum well (MQW) electronic states along @GAMMA@-barX-bar in the systems Cu/fccM(100) where M = Ni, Co, Fe. The model predicts that MQW states disperse with a high effective mass in regions of the 2-dimensional Brillouin zone where projected band gaps occur in the ferromagnetic material. Such regions occur near the belly and neck of the Cu Fermi surface. Near the belly, the regions of high effective mass will be observed below the Fermi energy (E@sub F@) for all three systems. Flat dispersions near the neck will occur about 1eV below the Fermi energy for Ni, about 1eV above E@sub F@ for Fe, and will pass through E@sub F@ for Co. These calculations give a good account of direct and inverse photoemission measurements from Cu/fccCo(100). We have recently performed inverse photoemission on Cu/fccFe(100) and Cu/fccNi(100) and the dispersions of the MQW states in these systems will be discussed and compared with the predictions of the phase accumulation model. Furthermore, there is evidence of parallel, flat MQW bands both below and above the Fermi level in the hybrid Cu/Fe/Cu/Ni system which indicate a possible optical resonance. This work was funded by the NSF, grant no. DMR98-01681 and the Petroleum Research Fund, grant no. ACS-PRF-33750-AC6,5.

4:00pm **MI-TuA7 Photoemission Study of Pseudomorphic Fe@sub x@Ni@sub 1-x@ and Co@sub x@Ni@sub 1-x@ Films on Cu(100)**, ***M. Hochstrasser***, The Pennsylvania State University, U.S.; *N. Gilman, R.F. Willis,* The Pennsylvania State University; *F.O. Schumann, J.G. Tobin,* Lawrence Livermore National Laboratory; *E. Rotenberg,* Lawrence Berkeley National Laboratory (Advanced Light Source)

The k-space electronic structure of Fe@sub x@Ni@sub 1-x@ and Co@sub x@Ni@sub 1-x@ alloy films epitaxially grown on Cu(100) has been investigated with changing stoichiometry in angle-resolved photoemission and is compared to the electronic structure of fcc films of Co and Ni, as well as of Cu. We have monitored changes in the Fermi surface with changing stoichiometry and changing magnetic behavior. In the bulk, the magnetic moment deviates strongly from the Slater-Pauling curve at an Fe concentration of 65%, dropping quickly to zero as does the Curie temperature, at which point a structural phase transition from fcc to bcc is observed. Recently, it has been shown that Fe@sub x@Ni@sub 1-x@ films can establish in the fcc phase when grown as ultrathin films on Cu(100).@footnote 1@ The fcc to bcc structural transformation is quenched, but the magnetic instability persists. Furthermore, we investigated with spin-resolved photoemission spectroscopy the regions relevant for the magnetic coupling with changing composition in Fe@sub x@Ni@sub 1-x@ films on Cu(100). We adress the questions: 1. Is there a relationship between the electronic structure and the sudden change in magnetization at a critical composition? 2. How does the Fermi surface evolve in these pseudomorphic alloy films? 3. What is the polarization of the states thought to be responsible for the oscillatory exchange coupling? The measurements show that the sp-band is a prominent feature of the Fermi surface throughout k-space for all of these alloys. A band structure calculation of Ni allows us to identify d-hole pockets arising from holes in the d-band(s) increasing with changing stoichiometry. The states thought to be responsible for the oscillatory exchange coupling, giving rise to giant magentoresistance (GMR) effects, are identified. @FootnoteText@ @footnote 1@ F. Schumann et. al., Phys. Rev. B, 56, 2668 (1997).

4:20pm **MI-TuA8 Magnetic Properties of Fe-based Alloys**, ***F.O. Schumann***, *J.G. Tobin,* Lawrence Livermore National Laboratory

The magnetic properties of fcc Fe@sub x@Ni@sub 1-x@ and Fe@sub x@Co@sub 1-x@ alloys grown on Cu(100)were investigated in an element-specific fashion.The technique employed was linear dichoism in photoemission (MLDAD), which by varying the chirality can also determine the magnetization axis. We observed a different behavior for the two alloys at Fe concentrations above 60%. At this concentration the Fe@sub x@Ni@sub 1-x@ alloy shows a strong reduction of the Fe dichroism associated with the invar instability.@footnote 1@ This is in contrast to the Fe@sub x@Co@sub 1-x@ alloy, where the Fe dichroism stays essentially constant across the concentration.This would indicate that a volume-moment instability is absent, which disagrees with a recent theoretical study.@footnote 2@ Despite these differences both systems show a change of the easy axis at roughly the same electron count.For small Fe concentrations the easy axis is in-plane along the [110] direction. This changes into the [100] direction at Fe@sub 60@Ni@sub 40@, which is at 0.8 excess electrons per atom when compared with Fe.This is different to the bulk, where a change occurs at Fe@sub 35@Ni@sub 65@. We find the easy axis change for Fe@sub x@Co@sub 1-x@ to occur at 35% Fe. This would be equivalent to 0.65 excess electrons when compared with Fe. @FootnoteText@ @footnote 1@ F.O. Schumann et al., Phys. Rev. Lett 79,5166 (1997). @footnote 2@ P.James et al., Phys. Rev. B 59,419 (1999).

Manufacturing Science and Technology Group
Room 611 - Session MS-TuA

Interconnect and Integration

Moderator: S. Shankar, Intel, Inc.

2:00pm **MS-TuA1 CD Control Optimization Methodology on Shallow Trench Isolation Substrate for Sub-0.25µm Technology Gate Patterning**, *M.H. Fan,* ***H. Gerung***, *P. Yelehanka, A. Cheng, M.S. Zhou, C. Chi,* Chartered Semiconductor Manufacturing Ltd., Singapore; *C.H. Tan, J. Xie,* Institute of Microelectronics, Singapore

The impact of post-Shallow Trench Isolation (STI) Chemical Mechanical Polishing (CMP) on gate critical dimension (CD) control for submicron technology had been studied. The response of the gate CD depends upon STI process scheme whether it is recess (STI lower than active) or elevated (STI higher than active). Two subjects had been studied: first, CD uniformity as the function of STI step height with active and secondly, CD uniformity as the function of the size of the active area. The topology step height and active size affect the resist coating and organic BARC thickness uniformity. BARC thickness uniformity affects the substrate reflectivity, which leads to variation in the effective exposure dose. This dose variation leads to CD swing across the wafer and resulting in non-uniform CD. We used AFM surface scan to study the topographical variations caused by CMP process on different active area size. A new simulation technique using topographical swing curves and CD error contour plot was applied in this work to optimize BARC and resist thickness. Prolith/2 from FINLE was used for process simulation and excellent agreement was found between simulation and experimental results. Better CD control can be achieved by avoiding extreme recessed or elevated STI topology.

2:20pm **MS-TuA2 Patterning of Xerogel in High Density Fluorocarbon Plasmas**, ***T.E.F.M. Standaert***, State University of New York at Albany; *C. Hedlund,* Uppsala University, Sweden; *E. Joseph, G.S. Oehrlein,* State University of New York at Albany; *W.N. Gill, P.C. Wayner, J.L. Plawsky,* Rensselaer Polytechnic Institute

The upcoming generations of integrated circuits will employ low dielectric constant (k) materials as interconnect isolation. Compared to conventional oxides, low k materials contribute less to circuit delays. Porous spin-on-glasses (k<2.5), e.g. Xerogel, are of particular interest for high speed devices. We present a detailed study on the patterning of Xerogel films with a porosity varying from 64% to 83%. The films were etched in a high density plasma tool using fluorocarbon gases. This allows for a high etch rate. For example, the etch rates in a CHF@sub 3@ discharge of a 78 % porous Xerogel film and a thermal oxide film are 2750 and 400 nm/min, respectively. The high etch rates can only partially be explained by the porosity of the films. Namely, the etch yield (number of atoms removed per ion impact) varies with porosity. For example, the yields in a CHF@sub 3@ discharge of a 78% porous Xerogel film and a thermal oxide film are 0.88 and 0.58, respectively. One possible explanation for this difference are residual organic groups present in the Xerogel films. We have also characterized the surface modifications after a partial etch by X- ray Photoelectron Spectroscopy (XPS). Finally, we compare the patterning of the Xerogel films to thermal oxides.

2:40pm **MS-TuA3 Surface Science of Tungsten CMP Removal**, ***D.J. Stein***, *D.L. Hetherington,* Sandia National Laboratories; *J.L. Cecchi,* University of New Mexico

Chemical mechanical polishing (CMP) is the predominant method for planarization and metal damascene processing during manufacture of submicron integrated circuits (IC). Tungsten CMP is used to remove excess tungsten after non-selective chemical vapor deposition in contacts and vias. We have investigated possible mechanisms of tungsten removal under typical IC manufacturing conditions. Previous models for tungsten CMP tungsten suggested that the dominant removal mechanism was the formation of a blanket oxide which was removed by mechanical abrasion.@footnote 1@ We used an electrochemical cell that allowed measurements of the tungsten oxidation rate and the removal rate. We found that the oxidation rate was between 0.01 and 0.1 of the tungsten removal rate, indicating that blanket oxidation does not play a significant role in tungsten removal.@footnote 2@ To elucidate the mechanisms responsible for tungsten removal, we undertook a number of additional investigations, including AFM and TEM imaging, correlations of the polish rate and process temperature dependence with the slurry constituent concentrations, and in-situ measurement of the friction and adhesion between the slurry colloid and the tungsten surface.@footnote 3,4@ We interpret our data with a heuristic model.@footnote 5@ It is shown that the empirical form of the heuristic model fits all of the data obtained. The mechanism also agrees with the limiting cases that were investigated. This mechanism captures the observed relationship between polish rate, pressure, velocity, and slurry chemistry. @FootnoteText@ @footnote 1@F. B. Kaufman et al., J. Electrochem. Soc. 138, 3460, 1991. @footnote 2@D. Stein et al., J. Electrochem. Soc. 145, 3190, 1998. @footnote 3@D. Stein et al., J. Electrochem. Soc. 146, 376, 1999. @footnote 4@D. Stein et al., submitted to J. Mater. Res. @footnote 5@D. Stein et al., accepted for publication in J. Electrochem. Soc.

3:00pm **MS-TuA4 Yield Improvement Through Multizone Uniformity Control of a CMP Process Utilizing a Pre and Post-Measurement Strategy***, **J. Moyne**, K. Khan,* University of Michigan*; J. Colt, J. Chapple-Sokol, R. Nadeau, P. Smith,* IBM*; T. Parikh,* SEMATECH **INVITED**

Achieving good uniformity process control in Chemical Mechanical Polishing (CMP) requires a representative uniformity metric and strong models relating this metric to process tunable inputs. Previous efforts in CMP uniformity control have yielded acceptable results utilizing a Center-to-Edge (CTE) first order non-uniformity metric. Closer analysis of post CMP process non-uniformity, however, reveals significant higher order non-uniformity components such as the center "dimple" and outer "doughnut" regions. These non-uniformity characteristics are due in large part to upstream CVD processing. Utilizing a multi-zone approach to uniformity modeling, a more accurate mathematical model of CMP uniformity has been identified. An optimization function has been developed based on minimizing the removal profile slopes as well as the absolute value of the area under the removal curve. The model and function have been utilized to customize a thickness and uniformity multivariate run-to-run software control solution for the process. The controller is based on the Generic Cell Controller structure, which is a proven enabler for run-to-run control for a number of processes including CMP, vapor phase epitaxy, and etch. The control algorithm is a zero'th order adjustable linear approximation two-stage algorithm with EWMA noise filtering. This algorithm, which supports first order linear and non-linear models, has been demonstrated to be effective in CMP CTE and thickness multivariate control. The control solution has been enhanced to utilize both pre and post CMP process metrology along with process models to suggest process recipe modifications on a run-to-run basis. Results indicate improved control of CMP process non-uniformity qualities of interest. Further, the results quantify the significant benefit of utilizing pre-metrology (feedforward) information in addition to traditional post metrology (feedback) in determining control recipe advices.

3:40pm **MS-TuA6 Modeling, A Tool for Technology Development***, **J.L. Garcia-Colevatti**,* Intel Corporation **INVITED**

Technology CAD, TCAD, is a term that describes a collection of model-based tools and methodologies that are used to assist process technology development, IC manufacturing control and the coupling of process specific behavior to products design. Different levels of model complexity, physics content and accuracy are needed depending on the development stage of a particular technology. The continuos need to understand and solve ever more difficult problems rapidly without escalating costs has forced us to draw and integrate results from multiple disciplines, enabling us to keep up with the relentless pace of silicon technology evolution. This presentation will review the scope of these tools, the infrastructure required for their rapid development and deployment and the benefits that result from their application to the exploration, development and manufacturing of new process technologies.

4:20pm **MS-TuA8 Simulations of TiN Barrier Films Deposited by I-PVD on High Aspect Ratio Features: Macrostructure and Composition***, M. Li, **S.K. Dew**, M.J. Brett,* University of Alberta, Canada*; T.J. Smy,* Carleton University, Canada

TiN films are extensively used as barrier layers for aluminum, tungsten, as well as copper in modern VLSI metallization processing. However, the properties of TiN are significantly dependent upon the microstructure and composition of the film. Physical vapor deposition is a technology commonly adopted for TiN barrier deposition, but recently the ionized variant, I-PVD, has attracted interest for deep sub-micron processes. In this work, by considering the adsorption and desorption of ionic and neutral nitrogen species, N and N2, and the reflection within the micro-features, the film growth simulator, GROFILMS, is used to study the film microstructure and composition over high aspect ratio topography in an I-PVD system. The effects of the film deposition conditions such as the total titanium flux, fraction of titanium ions, partial pressure of nitrogen, degree of nitrogen dissociation, substrate bias and film deposition temperature are investigated. In particular, the simulations demonstrate that ion impact energy and surface diffusion are two major processes determining the properties of TiN barrier films through control of the film density.

4:40pm **MS-TuA9 Investigation of Si and SiO@sub 2@ Etch Mechanisms Using an Integrated Surface Kinetics Model@footnote 1@***, **D. Zhang**, M.J. Kushner,* University of Illinois, Urbana

Computer aided development of new plasma etching processes requires a fully integrated plasma equipment and surface chemistry model to account for the interaction between bulk and surface processes. This is particularly important when different surfaces in the reactor (i.e., wafer, photoresist, walls, window) react differently with plasma generated species. To address these plasma-surface interactions throughout the etch chamber, and their influence on bulk plasma properties, the Surface Kinetics Model (SKM) was developed and integrated into the Hybrid Plasma Equipment Model (HPEM), a 2-D plasma plasma simulation tool. The SKM simulates the surface coverage and reactions of surface residence species using the flux of reactants from the HPEM. Ion energy and passivation layer thickness dependent processes are included. Patterned wafers can be addressed by partitioning the surface sites. The SKM was used to investigate the surface reaction mechanism for the fluorocarbon etching of SiO@sub 2@. The model includes formation of a passivation layer by CF@sub x@ radicals, its etching by F atoms and its sputtering by ions. The SiO@sub 2@ etch process is represented by 3 (or more) steps, which starts with formation of a CF@sub x@-SiO@sub 2@ complex which, with ion-energy activation, desorbs CO@sub x@ or COF@sub x@ products which diffuse back through the passivation. The remaining =SiF@sub x@ surface site is successively passivated by F atoms diffusing through the passivation, until ion activation desorbes the SiF@sub x@. Results will be discussed for C@sub 2@F@sub 6@ etching of SiO@sub 2@ in inductively coupled, rf biased reactors as a function of ICP and bias power, demonstrating the dependence of etch rates and selectivity on passivation layer thickness. @FootnoteText@ @footnote 1@This work was supported by SRC and LAM Research.

5:00pm **MS-TuA10 Design of a Dual Frequency PECVD Reactor for Advanced Integrated Circuits Processing***, **S. Raoux**, M. Mudholkar, W.N. Taylor, M.A. Fodor, J. Huang, D. Silvetti, K. Fairbairn,* Applied Materials

A capacitively-coupled PECVD reactor was designed using a high-temperature AlN ceramic heater with an embedded RF electrode. The first electrode (at the wafer) is biased at low frequency (350kHz) to control ion bombardment during film growth. The second RF electrode (or showerhead) is biased at 13.56MHz and has conical holes providing a (soft) hollow cathode effect for intense molecule dissociation and ionization efficiency. In this paper, we present advances in Si3N4 film deposition using a dual frequency RF plasma and SiH4, NH3 and N2 as precursor gases. We investigate the relation between ion energy and dual frequency plasma impedance, and correlate plasma potential with the film density and etch integrity. A SPICE (Simulation Program with Integrated Circuits Emphasis) model of the plasma reactor was determined. The model is compared to experimental data, and it is shown that the film stress is correlated to the phase angle (I/V) of the low frequency bias and to the heater electrode capacitance. We will present applications of this reactor for deposition of low-temperature (400C) Inter-Metal-Dielectric films and High Temperature processes (550C) for Pre-Metal-Dielectric films.

Nanometer-scale Science and Technology Division
Room 612 - Session NS-TuA

Innovative Nanoscale Measurements

Moderator: E.T. Yu, University of California, San Diego

2:00pm **NS-TuA1 Size, Shape, Strain, and Composition Inhomogeneities of In@sub 0.5@Ga@sub 0.5@As QDs Grown by Migration Enhanced Epitaxy***, **N. Liu**, C.K. Shih, O. Baklenov, A.L. Holmes, Jr.,* The University of Texas at Austin

We report cross-sectional scanning tunneling microscopy (XSTM) studies of In@sub 0.5@Ga@sub 0.5@As self-assembled quantum dots (SAQD) grown using migration enhanced epitaxy (MEE). Samples were cleaved in-situ to reveal either (110) or (1-10) cross-sectional surfaces. For the 10 ML QDs, they exhibit truncated-pyramid shapes with well-defined facets on both (110) and (1-10) projections. On the (110) surface, the orientation of the facets is about 35 degrees with respect to the base of the QDs, and on the (1-10) surfaces about 25 degrees with respect to the base. The average height of the 10 ML QDs is about 10 nm, while the average base length is about 45 nm along the (110) projection and about 61 nm along the (1-10) projection. We further discovered that the In-concentration in this kind of truncated-pyramid shaped QDs is inhomogeneous. In fact the qualitative concentration contours at high concentration show an inverted triangle shape. Similarly the distribution of the lattice parameters (as determined from the STM) within and around the QD is also inhomogeneous with its inhomogeneity consistent with an inverted triangle shape of high In-concentration in the QD. Detailed analysis and possible mechanism responsible for such a concentration distribution profile will be discussed.

2:20pm **NS-TuA2 Cross-Sectional Scanning Tunneling Microscopy as a Probe of Atomic-Scale Order in MOVPE Grown GaInP@footnote 1@***, J. Steinshnider,* *M. Weimer,* Texas A&M University*; M. Hanna,* National Renewable Energy Laboratory

III@sub a@-III@sub b@-V alloys grown by metal-organic vapor phase epitaxy (MOVPE) exhibit varying degrees of CuPt-B order in which III@sub a@ and III@sub b@ atoms preferentially enrich alternating -B planes during growth to form a monolayer superlattice. We have used cross-sectional scanning tunneling microscopy (STM) to examine and characterize spontaneous ordering in MOVPE-grown GaInP films lattice-matched to GaAs. We show how cross-sectional STM permits the direct, real-space visualization of CuPt order based on III@sub a@-III@sub b@ site discrimination, and indicate how the degree of local order in selected regions of a sample may be quantitatively assessed through the In-In pair correlation function constructed from atomic-resolution data. We introduce a local order parameter, based on the pair correlation function, that is identified with the Bragg-Williams parameter in the case of long range order and which allows a direct comparison of the STM results with optical or x-ray measurements. We have examined the spatial evolution of the local order parameter in the vicinity of the alloy / buffer interface, where the STM images show evidence for atomically-abrupt antiphase boundaries, and find that the onset of recognizable group-III sublattice order requires approximately twenty monolayers. The ability of cross-sectional STM to probe the development of local order on these length scales suggests it will be a powerful tool for studying the mechanism of atomic ordering as well as optimizing the growth of ordered films. @FootnoteText@ @footnote 1@Work supported in part by a grant from the National Science Foundation, Division of Materials Research.

2:40pm **NS-TuA3 Interpreting Atomic-Scale Structure in Cross-Sectional STM Images of III-V Superlattices***, W. Barvosa-Carter,* ***B.Z. Nosho****, M.J. Yang, L.J. Whitman,* Naval Research Laboratory

Cross-sectional scanning tunneling microscopy (XSTM) is a powerful method for quantifying the structural and interfacial quality of III-V semiconductor superlattice structures. Although a variety of III-V systems have been studied with XSTM, there are a number of aspects related to image interpretation, particularly on the atomic-scale, that are still a matter of discussion. One rarely discussed issue is that on the (110) cleavage face only every other III-V growth layer within the superlattice can be directly observed by XSTM. This fact can have important consequences when investigating properties of the superlattice such as the roughness between heteroepitaxial layers, interfacial defects, or variations in chemical bonding at the interface. The impact is especially significant when these effects occur predominantly within a volume only two to three monolayers (ML) wide. We are systematically investigating the appearance of III-As and III-Sb bonds at arsenide-antimonide interfaces as a function of cleavage direction and even-versus-odd layers in specially prepared MBE-grown superlattices. We find it is possible to differentiate between the two bond types, but their appearance depends on cleavage-face and layer order. In addition, a model of the measurement of interfacial roughness reveals errors in the measured power spectrum as the actual interface roughness decreases below 2 ML. A simple method for reconstructing the actual power spectrum from the STM data will be described. Funded by the Office of Naval Research and the Air Force Research Laboratory. Present address for W. Barvosa-Carter is HRL Laboratories, Malibu, CA.

3:00pm **NS-TuA4 The Importance of Many-body Effects in the Clustering of Charged Zn Dopant Atoms in GaAs***,* ***Ph. Ebert,*** Forschungszentrum J@um u@lich, Germany*; T.-J. Zhang,* University of Tennessee*; F. Kluge, M. Simon,* Forschungszentrum J@um u@lich, Germany*; Z. Zhang,* Oak Ridge National Laboratory*; K. Urban,* Forschungszentrum J@um u@lich, Germany

The spatial distribution of negatively charged Zn dopant atoms in GaAs has been investigated by cross-sectional scanning tunneling microscopy. At high densities, the dopant atoms exhibit clear clustering behavior, suggesting the existence of an effective attractive interaction in addition to the screened Coulomb repulsion between two dopants. By analyzing the data through Monte Carlo simulations, we have extracted the intrinsic screening length at different dopant densities, and attributed the origin of the effective attraction to strong many-body effects in the dopant-dopant repulsion.

3:20pm **NS-TuA5 New Methods to Measure Electrical, Optical, and Magnetic Properties on the Nanometer Scale***,* ***M. Aono,*** Osaka University and Institute of Physical and Chemical Research, Japan **INVITED**

In order to measure electrical, optical, and magnetic properties of materials on the nanometer scale, we have developed (a) a scanning tunneling microscope (STM) that has three tips operated independently, (b) a photon-detecting STM equipped with a polari zation analyzer, and © a spin-polarized STM with a nonmagnetic high-Z material tip, respectively. In the present paper, we show selected experimental results obtained with these apparatuses. Also we would like to show interesting experimental results on local polymerization of organic molecule in monolayer films. They include chain polymerization of diacetylene compound molecules triggered by a STM tip.

4:00pm **NS-TuA7 Field Dependent Electric Potential Gradients at Atomically Abrupt Oxide Interfaces***,* ***D.A. Bonnell,*** *B. Huey, S. Kalinin,* University of Pennsylvania

Scanning Surface Potential Microscopy has been used to measure spatial variations in electric fields near atomically abrupt interfaces in SrTiO@sub 3@ and ZnO. The field dependence of potential gradients is determined by using microlithography to isolate regions of the interface and apply local electric fields during the measurements. The local potential drop is used to determine the interface density of states. A procedure for extracting actual interface potential from separation dependence is proposed.[100] symmetric tilt boundaries in SrTiO@sub 3@ with tilt angles ranging from 15°-60° are examined and interface potential is related to atomic structure.

4:20pm **NS-TuA8 Dynamics of Adsorbate Islands with Nanoscale Spacial Resolution: (OH)@sub n@ Formation during the NO/H@sub 2@ Reaction on Pt(001)***, C. Voss, T. Visart de Bocarmé, T. Bär,* ***N. Kruse,*** Université Libre de Bruxelles, Belgium

Studies by Field Ion Microscopy (FIM) of the catalytic NO hydrogenation (p@sub H2@ = 4 x 10@super -3@ Pa and p@sub NO@ = 3 x 10@super -3@ Pa at 500 K) on the (001) plane of a Pt tip have resulted in the observation of small islands with a size corresponding to 10-30 Pt surface atoms. Simultaneous atom-probe work allowed these islands to be consistently interpreted as being due to the intermediate formation of hydroxyl species in an O@sub ad@/H@sub ad@ coadsorbed layer. Imaging of this reaction phenomenon was achieved by field ionisation of NO at field strengths slightly above those usually present in Scanning Tunneling Microscopy (STM). OH@sub ad@ islands exclusively formed at the layer edge with subsequent movement into the (001) terrace region. Usually one to two islands were observed at the same time with no mergence occurring on collision. Mean lifetimes of several minutes were observed for individual islands before their annihilation at the layer edge. The formation of OH@sub ad@ clusters must be regarded as a collective reaction phenomenon involving a delicate balance of attractive and repulsive forces between adspecies. The results will be presented in a video sequence and compared to a sucessful computer simulation with an automaton lattice model.

4:40pm **NS-TuA9 Measuring Average Tip-sample Forces in Intermittent-contact (Tapping) Force Microscopy in Air***,* ***S.C. Fain, Jr.,*** *K.A. Barry, M.G. Bush, B. Pittenger,* University of Washington*; R.N. Louie,* Pacific Lutheran University

Many soft substances such as polymers and biological molecules show much less damage when imaged with intermittent-contact (tapping) force microscopy; however, the tip-sample forces involved have never been directly measured. The mathematical solutions to the non-linear differential equations needed to calculate these forces can be extremely complicated even for mass-on-a-spring models. In these experiments piezoresistive cantilevers (from Park Scientific/ ThermoMicroscopes) are used to measure the average force on a silicon surface produced by the silicon tip of a separate mechanically-driven (active) cantilever. The procedure consists of slowly moving the two cantilevers toward and away from each other while measuring as a function of the change in distance between the two support points: the average deflection of the piezoresistive cantilever, the amplitude of the active cantilever, the change in phase of the active cantilever relative to the mechanical driver, and the change in the average deflection of the active cantilever. Recent simulations by Garcia and San Paulo (Phys. Rev. B., in press) predict the force exerted on a model substrate averaged over a complete cycle, the amplitude, and the phase shift as a function of distance; they find that the force starts to rise when the phase shift indicates repulsive tapping. These predictions are compared with our measurements. The limit on the sensitivity of our average force measurements is set by the 1/f noise of the piezoresistive cantilever. This work was supported by NSF DMR 96-23590 and the UW Royalty Research Fund.

5:00pm **NS-TuA10 Imaging the Near-field Intensity Gradients with a Tapping-mode Near-field Scanning Optical Microscope***, **D.P. Tsai**, C.W. Yang,* National Chung Cheng University, Taiwan

A tapping-mode near-field scanning optical microscope system using a non-optical tuning fork method has been developed recently. One of the advantage of this new method is that tapping of the near-field optical fiber probe can provide the measurements of the near-field intensity gradients at different heights vertically. Based on the modulation of the near-field optical fiber probe, near-field intensity gradients were used as a new contrast mechanism of the NSOM. The imaging of the near-field field optical intensity gradients have been successfully applied on the study of both the propagating and evanescent field intensity. The propagating field with a constant intensity shows an image of zero gradients. The evanescent intensity gradients of the configurations of total international reflection or surface plasmons, on the other hand, indicate the local optical properties of the photon-matter interactions. Imaging contrast of the near-field optical intensity gradients of a focused spot on the clear cover glass slip and the gold-coated cover glass slip will be shown. Property of the local optical interactions of the gold thin film in near field was discerned. Results demonstrate the novelty of the imaging contrast of the near-field intensity gradients.

Organic Electronic Materials Topical Conference
Room 616/617 - Session OE+EM+AS-TuA

Organic Thin Film Growth

Moderator: H. Baessler, Philipps Universität, Germany

2:00pm **OE+EM+AS-TuA1 Tailoring of Properties of Organic Thin Films by Interface Control***, **E. Umbach**, M. Sokolowski, R. Fink,* Universität Würzburg, Germany **INVITED**

The properties of ultrathin organic films in organic/inorganic hybrid systems are largely determined by their interfaces. This is particularly true for the electronic and structural properties which depend on chemical bonding and ordering processes. In favourable cases weak chemisorption on smooth single-crystal surfaces leads to long-range lateral order, and even true epitaxial growth of organic overlayers can be achieved. For such structurally well-defined films significantly improved transport and optical properties can be expected. It will be shown how high-quality organic thin films can be prepared by vapour-deposition on suited substrates and how the observed superstructures depend on the molecular shape and the functional groups, on the substrate material and orientation, and on the preparation parameters. Moreover, based on a few examples it is demonstrated that epitaxial growth with huge domains and even with new, substrate-induced structural parameters can be achieved. In view of their optical properties, for instance, such films show very few defects, considerably improved quantum efficiency, and reduced substrate-induced quenching. The knowledge about the various properties and their interdependences has been achieved by combining a number of surface-sensitive methods for studying the geometric (STM, (SPA)LEED), chemical (XPS, TDS, HREELS), orientational (NEXAFS), and electronic (UPS, NEXAFS) properties with in-situ measurements of the optical and electric properties. As substrates different metal (e.g., Ag, Ni, Cu) and semiconductor surfaces (Si, Ge, ZnSe, HOPG) have been investigated, and the properties of more than 20 different large organic molecules have been compared. On the basis of the present results one can now start to tailor the properties of ultrathin organic films by selecting a proper combination of molecules, substrates and preparation conditions.

2:40pm **OE+EM+AS-TuA3 Ordering in Two Dimensions - Phthalocyanines, Perylenes, and Related Molecular Thin Films***, **N.R. Armstrong**,* University of Arizona **INVITED**

Well-ordered two-dimensional thin films can now be routinely produced by either vacuum deposition and/or self-assembly deposition technologies, and rules for epitaxial growth of such materials on a variety of single crystal substrates are becoming well understood. This talk will review recent work on the growth of both phthalocyanine and perylene dye thin films, on both single crystal metal and nonmetal surfaces. Many of the crystalline organic dyes tend to form flat-lying ordered monolayers, with coincident epitaxial relationships with the substrate. Several interesting cases have recently emerged, however, where such flat-lying monolayers are not formed, and/or where neither coincident nor commensurate epitaxial structures are formed, but ordered films result nevertheless. In all events organic heterojunction formation is of interest for these materials, and characterization of such heterojunctions by combinations of XPS/UPS will be discussed. In addtion, we will discuss recent self-assembly approaches to ordered phthalocyanine thin films, by non-vacuum deposition approaches, which produce coherence in thin film structures rivaling the best vacuum deposited materials.

3:20pm **OE+EM+AS-TuA5 Influence of Steps on the Orientation of Monolayer Films of Copper Phthalocyanine (CuPc) on Au(111)***, **I. Chizhov**, A. Kahn, G. Scoles,* Princeton University

The structure of monolayer films of copper phthalocyanine (CuPc) deposited on Au(111) surface in ultrahigh vacuum is studied via scanning tunneling microscopy (STM) and low-energy electron diffraction (LEED). CuPc molecules adsorb with the molecular planes parallel to the surface and form a highly ordered overlayer with a square unit cell. The structure of the CuPc molecular layer is analyzed via correlation of STM and LEED data. The azimuthal orientation of the monolayer is found to be distinctly different on wide and narrow terraces of the Au(111) substrate. On wide terraces the azimuthal orientation of the monolayer is determined by the underlying substrate with the sides of CuPc square unit cells aligned within a few degrees off the [11(bar)0] and [112(bar)] directions of the Au(111) surface. On the other hand, on narrow terraces and in the vicinity of the Au substrate steps the sides of CuPc unit cells are aligned along the step edges. Thus, CuPc/Au(111) represents a good model system for which a balance between the energy of interaction of a molecule with the metal surface and that of interaction with the step edges can be studied in detail. For CuPc films with coverages below and above 1 monolayer no molecular structure can be reproducibly resolved by the STM.

3:40pm **OE+EM+AS-TuA6 Growth Modes of N,N'-bis-(1-naphthyl)-N,N'-diphenyl1-1,1-biphenyl1-4,4'-Diamine on Standard and Ultra-flat Indium Tin Oxide***, **E.W. Forsythe**, Q.T. Le, Y. Gao, L.J. Rothberg, M. Abkowitz,* University of Rochester

The ITO substrate morphology influences the growth conditions of N,N'-bis-(1-naphthyl)-N,N'-diphenyl1-1,1-biphenyl1-4,4'-diamine (NPB) for organic light emitting diodes. We have studied the growth modes of NPB on as-received indium tin oxide (ITO) and ult ra-flat ITO using atomic force microscopy (AFM). The ITO surface morphology has been reduced from an average area roughness of 1.8nm to less than 0.2nm with clearly distinguishable atomic terraces corresponding to the ITO lattice spacing. The room temper a ture NPB growth mode is initially islands with complete ITO coverage at 15nm for both ITO surfaces. With a substrate temperature less than 15C above room temperature, the growth modes are laminar with full ITO coverage at 7.5nm. The final NPB film on t h e ultra-flat ITO has an average roughness equivalent to the size of the NPB molecule, more than an order of magnitude less than NPB on standard ITO. Because NPB is trap free, a direct and self-consistent measure of the injection efficiency as a function IT O surface morphology and growth temperature can be determined at a given applied field from the ratio of the measured dark current to the calculated trap free space charge limited current. The trap free space charge limited current is calculated from t h e t ime of flight drift mobility measured in the same specimen at the same applied field.@footnote 1@ The OLED device performance shows an approximately 15% increase in the cd/A efficiency on the ultra-flat ITO as compared to standard ITO. Understandi ng t he role of the ITO surface morphology on OLED device characteristics may contribute to improved large area device performance. This work was supported by DARPA DAAL01-96-K-0086, NSF DMR-9612370, AFOSR 96NL245, and the NSF Center for Photoinduced Charge Transfer. 0. @FootnoteText@ @footnote 1@ M.Abkowitz,J.S.Facci and J.Rehm. J. Appl. Phys. 83, 2670 (1998).

4:00pm **OE+EM+AS-TuA7 Self-Assembled Monolayers on Indium Tin Oxide***, C. Yan, M. Zharnikov, **A. Gölzhäuser**, M. Grunze,* Universität Heidelberg, Germany

Self-Assembled Monolayers (SAMs) of functionalized alkanethiols X(CH@sub 2@)@sub n@SH (X=CH@sub 3@, COOH) and carboxylic acid CH@sub 3@(CH@sub 2@)@sub n@COOH were prepared on indium tin oxide (ITO) surfaces and have been characterized by X-ray photoelectron (XPS) and Near Edge X-ray Absorption Fine Structure (NEXAFS) spectroscopies as well as by Atomic Force Microscopy (AFM). Thiols as well as carboxylic acids form homogeneous, ordered films on ITO. NEXAFS data suggest that the films are molecularly oriented with average alkyl chain tilt angles between ~34° for thiolate and ~31° for bifunctional SH(CH@sub 2@)@sub 15@COOH. From coadsorption experiments we find that on ITO the COOH group adsorbs preferentially over the SH group. AFM and LFM images indicate a smoothing of the relatively rough ITO surface by the adsorbed films. These results suggest that ITO surfaces can be passivated with Self-assembled monolayers and that SAMs can be utilized to covalently attach specific chemical functionalities to ITO electrodes.

4:20pm **OE+EM+AS-TuA8 Mechanism of Formation of Self-Assembled n-Octadecylsilane Monolayers on Indium-Tin-Oxide***, **K.-W. Lee**, A.M. Raphel, S.L. Buchwalter,* IBM T.J. Watson Research Center*; M.M. Poliks,* IBM Microelectronics

Mechanism of formation of self-assembled n-octadecylsilane monolayers on indium-tin-oxide (ITO) has been studied. n-Octadecyltrimethoxysilane (OTMS) was hydrolyzed to n-octadecylmethoxysilanediol or n-octadecylsilanetriol in isopropanol/water (95/5). The 0.5 % hydrolyzed solution was spin-coated onto ITO substrate and then baked at 85 deg.C for 30 min. The subsequently formed organic layers were analyzed with dynamic contact angles, X-ray photoelectron spectroscopy (XPS) and reflection-absorption infrared spectroscopy (RAIR) and determined to have densely packed SAMs. Its RAIR and XPS spectra indicate that lots of silanol groups are left unreacted at the foot of SAMs and a small amount of unhydrolyzed Si-OCH3 groups may also be present. Silanol groups are expected to interact with each other and ITO surface through hydrogen bonding. The distance between Si atoms can be long enough to have a normal tilt angle (app. 30 deg.) of typical SAMs. Si-OH and Si-OCH3 groups were fully condensed to polysiloxane by further thermal treatment at 230 deg.C for 30 min, as evidenced by the disappearance of the O-H band in RAIR as well as by the decrease of the O1s band corresponding to silanol. The possible structural changes in the SAM driven by this condensation are discussed. In contrast to the fully hydrolyzed OTMS solution, a partially hydrolyzed OTMS solution provided loosely packed monolayers, apparently in islands of densely packed alkyl chains rather than as monotonically diminishing coverage.

4:40pm **OE+EM+AS-TuA9 Growth and Characterization of Poly(arylamine) Thin Films Prepared by Vapor Deposition***, **G.J. Szulczewski**, T. Selby, S. Blackstock,* The University of Alabama

We have synthesized a novel series of redox-gradient poly(arylamines) dendrimers for potential applications in organic-based electronic devices. The thermal properties of these materials have been measured by gravimetric analysis and differential scanning calorimetry. In general, these materials exhibit a glass transition temperature near 100 C and show negligible weight loss below 400 C. Thin films (1-100 nm) of these materials were grown under high vacuum conditions by vapor deposition onto a variety of substrates, including: gold, Si(100), and indium-tin oxide coated glass. Ex situ surface characterization was performed with reflection-absorption infrared spectroscopy, x-ray photoelectron spectroscopy, spectroscopic ellipsometry, and atomic force microscopy. These analyses show the formation of high quality films from the organic precursors with molecular weights exceeding 1300 amu without molecular decomposition. Thus, a new class of functional organic films for potential use in charge storage and transport have been prepared. The efficacy of these films as hole transport materials in electroluminescent devices and charge storage media is under current investigation.

5:00pm **OE+EM+AS-TuA10 HREELS Study of Ultra-thin Polyaniline Films Grown on Cu(110) by Vapor Deposition of Aniline Tetramers***, **K.K. Lee**, J.M. Vohs,* University of Pennsylvania*; N.J. DiNardo,* Drexel University

Substrate-dependent reactivity, thin film polymerization, and metallic conductivity upon doping have been demonstrated in previous HREELS studies of vapor-deposited emeraldine thin films on metal surfaces.@footnote 1@ In those studies, the chemical vapor was composed of a distribution of oligomeric sizes. In this HREELS study, the effect of the size of vapor-deposited oligomers on the growth of polyaniline at a metal surface is addressed through deposition of aniline tetramers on Cu(110). Analysis of vibrational and electronic spectra for growth up to ~70 Angstroms shows polymerization reactions with shorter chain lengths of the resulting polyaniline ultra-thin films than for deposition from emeraldine vapor. Upon doping, the far-infrared region exhibits intense tailing and a plasmon loss indicating that local conductivity is similar to ultra-thin films composed of longer chains. @FootnoteText@ @footnote 1@K. K. Lee - Surf Sci. 420 (1999) L115 and references therein.

Plasma Science and Technology Division
Room 609 - Session PS-TuA

Plasma Diagnostics II

Moderator: M.G. Blain, Sandia National Laboratories

2:00pm **PS-TuA1 Infrared and Microwave Absorption Diagnostics of Plasmas for Silicon Oxide Etching and Deposition***, **R.C. Woods**,* University of Wisconsin, Madison **INVITED**

Absorption spectroscopic diagnostics are non-invasive and provide absolute species concentrations, integrated along the radiation path. Infrared diode laser spectroscopy uses molecular vibration-rotational lines, while microwave spectroscopy looks at pure rotational lines of molecules. The sensitivity of both is high, and their high resolution permits unambiguous separation and identification of many species. We have recently used IR diode laser spectroscopy to measure CF, CF@sub 2@, and CF@sub 3@ absolute concentrations in an inductively coupled GEC etching reactor in G. Hebner's laboratory at Sandia N.L. The three species' densities were studied as functions of power and pressure in C@sub 2@F@sub 6@ and CF@sub 3@H discharges, over both blanket silicon and blanket photoresist wafers. A home built microwave spectroscopic diagnostic has similarly been used at Wisconsin to study concentrations of several species in ECR plasmas intended for deposition of silicon oxide or fluorinated silicon oxide. Gas mixtures studied are silane/oxygen and TEOS/oxygen, or these with admixture of SiF@sub 4@. Species detected by this technique include SiO, CF@sub 2@, SiF@sub 2@, SiF@super +@, and several TEOS oxidation products, e.g., methyl and ethyl alcohol, formaldehyde and acetaldehyde, and formic acid. Although in principle these two absorption spectroscopic techniques are very closely related, sometimes looking at the same molecules and even absorbing from the same quantum levels, each has its own advantages and limitations, and these will be briefly discussed here. This work was supported by National Science Foundation Grant #EEC-8721545 and by SEMATECH under contract no. 38010430.

2:40pm **PS-TuA3 Thomson Scattering with Gated Intensified CCD Detectors for Diagnostic of rf Discharge Plasmas***, **S.A. Moshkalyov**, T. Morrow, C. Thompson, W. Graham,* Queen's University of Belfast, Northern Ireland, UK

Thomson scattering (TS) with high-repetition rate lasers has been recently introduced as a diagnostic of electron parameters (electron density and electron energy distribution function, EEDF) in low-temperature gas discharge plasmas. This method has some distinct advantages over other techniques (like electric probes) which are commonly used to measure electron parameters in gas discharges. This technique is non-intrusive, and the interpretation of data is straightforward. However, due to the small cross-section of light scattering by free electrons, TS signals are extremely low (~ 20-30 photoelectrons/pulse for an electron density of 10@super 11@ cm@super -3@). To improve signal-to-noise ratios, measurements are typically made by accumulating the signals over ~10@super 3@ laser pulses. In most TS experiments, single-channel photomultiplier tubes are used for the light detection. A further step in the diagnostic development is the use of multichannel detectors such as gated intensified CCD's which record the entire TS spectrum and thus reduce considerably the time needed for measurements of the electron parameters. In our experiments, TS system with 10 Hz YAG laser (0.5 J at 532 nm) and a low-noise ICCD detector is used for diagnostics of an inductively coupled RF discharge plasma in a GEC reference cell. Experiments were carried out in Ar plasma for low pressures (25-250 mTorr) and relatively low powers (30-70 W). Experiments have shown that high accuracy of EEDF measurements in an extended range of electron energies (up to 12-15 eV) can be achieved by accumulating TS signals in 500-2500 pulses, with overall measurement time as small as 2-10 minutes. For high argon pressures EEDF has shown to be close to Maxwellian, while for low pressures strong deviation from Maxwellian distribution has been observed. The study of the effect of other gases admixtures to Ar is now on the way.

3:00pm **PS-TuA4 Determination of Electron Temperatures and Species Concentrations During Aluminum Etching***, **V.M. Donnelly**, M.V. Malyshev, S.W. Downey, J.I. Colonell, N. Layadi,* Bell Laboratories, Lucent Technologies

Electron temperatures (T@sub e@) and species concentrations were obtained in chlorine-containing, high-density, inductively coupled plasmas (Applied Materials decoupled plasma source (DPS) metal etcher), using trace rare gases optical emission spectroscopy (TRG-OES). Measurements were carried out as a function of total pressure, source power, fraction of BCl@sub 3@ added to Cl@sub 2@ and substrate material (SiO@sub 2@, Al, and photoresist). A small amount (1.7% each) of all five rare gases was added to the plasma and emission spectra were recorded. TRG-OES T@sub e@ s corresponding to the high energy tail of the electron energy distribution function were derived from the best match between the observed and computed rare gas emission intensities. At source and bias powers of 1000 and 100 W, TRG-OES T@sub e@ s in Cl@sub 2@/BCl@sub 3@/N@sub 2@/rare gas plasmas increased from 1.5 eV at 40 mTorr to 3.0 eV at 3 mTorr, in good agreement with values computed from a global model and somewhat lower (at higher pressures) than those measured with a Langmuir probe. Surprisingly little dependence of T@sub e@ on substrate material was found. Reduced plasma induced damage at higher pressures correlated with a drop in both T@sub e@ and plasma density, but appears to be due mostly to the lower T@sub e@. Cl@sub 2@, Cl, BCl@sub 2@, BCl, B, AlCl@sub 2@, AlCl, Al, N@sub 2@ and BN emissions were identified. Qualitative, and in some cases quantitative absolute number densities were obtained by dividing these emission intensities by that from Ar, or Xe, corrected for electron impact excitation from Xe metastables.

3:20pm **PS-TuA5 Peter Mark Memorial Award Address***, **E.S. Aydil**[1],* University of California, Santa Barbara **INVITED**

4:00pm **PS-TuA7 Cavity Ring Down Spectroscopy for the Detection of Hydrocarbon Radicals during a-C:H Deposition***, **K.G.Y. Letourneur**, M.C.M. van de Sanden, R. Engeln, M.G.H. Boogaarts, D.C. Schram,* Eindhoven University of Technology, The Netherlands

Cavity Ring Down spectroscopy can be used in order to quantify the relative influence of radical species impinging on a growth surface. This enhanced absorption technique allows the determination of low species ground state densities as well as the evaluation of their rotational and vibrational temperature. It also allows for time and space resolved measurements. Cavity Ring Down spectroscopy has been applied during the deposition of hard hydrogenated amorphous carbon films obtained from a remote argon arc plasma in which acetylene is injected as carbon precursor. The C@sub 2@H@sub 2@ molecules are subsequently dissociated by argon ions and electrons, present in the plasma, producing hydrocarbon radicals (C@sub 2@H@super *@ and CH@super *@) responsible for deposition (rates up to 20 nm/s). However, hitherto, to the best of our knowledge, no direct detection of the ground state of those radicals has ever been reported in such environment. Detection of the ground state of the CH and C@sub 2@H radicals via CRD spectroscopy around 430 nm and 276 nm respectively are presented. Typical ground state densities of CH of around 10@super 17@ m@super -3@ are found. The results are used to develop a model for the deposition process of hydrogenated amorphous carbon from a remote plasma.

4:20pm **PS-TuA8 Characterization of Transformer Coupled Oxygen Plasmas by Trace Rare Gas-Optical Emission Spectroscopy and Langmuir Probe Analysis***, **N.C.M. Fuller**,* Bell Laboratories, Lucent Technologies and Columbia University*; M.V. Malyshev, V.M. Donnelly,* Bell Laboratories, Lucent Technologies*; I.P. Herman,* Columbia University

Trace rare gas-optical emission spectroscopy (TRG-OES) and Langmuir probe analysis have been used to measure the electron temperature, T@sub e@, in a high-density inductively (transformer) coupled (TCP) 10 mTorr oxygen plasma as a function of the 13.56 MHz radio frequency (rf) power. Rare gas actinometry and modeling at 7774 and 8446 Å have been used to determine the absolute densities of ground state atomic and molecular oxygen and the O(@super 1@D), O(@super 1@S) and O@sub 2@(a @super 1@@delta@@sub g@) metastables in the plasma. In the bright (inductive) mode, T@sub e@ increases from 2.7 to 3.4 eV for the electrons sampled by the Langmuir probe and from 4.1 to 5.5 eV for the high energy electrons sensed by TRG-OES, as rf power is increased from 100 to 1046 W. In the dim (capacitive) mode, below 45 W, T@sub e@ increases from a few eV at very low rf power to ~ 6 eV at 45 W. T@sub e@ decreases from 4.5 ± 1.5 eV at ~ 45 W to ~ 3.3 ± 0.8 eV at ~ 100 W. The gas dissociation peaks at ~ 40% at the maximum rf power density of 5.7 Wcm@super -2@ (1046 W), for which the ground state atomic and molecular oxygen concentrations are 2.5 x 10@super 14@ cm@super -3@ and 3.9 x 10@super 13@cm @super -3@ respectively. At this power density, the densities of O(@super 1@D) and O(@super 1@S) are 2.0 x 10@super 13@ cm-3 and 4.5 x10@super 11@ cm-3 respectively and the metastables collectively account for ~ 8% of all neutral species. For this power density, excitation of the metastables contribute ~ 44% and ~ 50% of the emission observed at 7774 and 8446 Å respectively, with the O(@super 1@D) metastable being the principal contributor. In the dim mode, the densities of O(@super 1@D) and O(@super 1@S) are three and five orders of magnitude smaller, respectively, than that of ground state atomic oxygen. Throughout the rf power range investigated, the density of O@sub 2@(a @super 1@@delta@@sub g@) is ~ one-third that of O(@super 1@D).

4:40pm **PS-TuA9 Diagnostics of Large-area Plasma Produced by Surface Waves on a Metal Wall with Periodicity***, **T. Yamauchi**, K. Aoki,* Toshiba Corporation, Japan*; H. Sugai,* Nagoya University, Japan

Surface-wave plasma is a promising next-generation plasma source since it readily yields a large-area high-density plasma at low pressures. In most cases, surface waves at 2.45GHz are excited along a dielectric wall, however, the use of a large-area dielectric wall often induces serious wall erosion and impurity release. To avoid such problems, the use of a metal wall with periodic structures which results in an increase in plasma density as well as an improvement in density uniformity is proposed in this paper. The top of the vacuum chamber consists of an Al plate(340mm diameter) comprising two quartz windows (20mm width) which also serve also serving as slot antennas. A periodic structure was installed on the Al plate. The experimental conditions are an Ar gas flow rate of 60sccm, a pressure from 30 to 70Pa and a microwave power of 2kW. We obtained the electron density of 10@super11@10@super12@cm@super-3@, which exceeds the cut off density (7.44 x10@super10@cm@super-3@)for 2.45GHz. The behavior of the ion saturation current, electron density and electric field intensity between two slots. Without the periodic structure the values show peaks under each slot antenna, thus indicating the influence of microwave radiation from the slot antennas themselves. Accordingly, it is revealed that the periodic structure on the metal wall is effective for generating a large-area surface-wave plasma.

5:00pm **PS-TuA10 UV Absorption Spectroscopy of Pulsed Fluorocarbon Plasmas***, **B.A. Cruden**, K.K. Gleason, H.H. Sawin,* Massachusetts Institute of Technology

Thin polytetrafluoroethylene(PTFE)-like films have been deposited in a pulsed capacitively coupled plasma from a variety of fluorocarbon precursors. It has been shown that pulsing of the plasma allows for composition control, giving reduced amounts of cross-linking and branching, and a higher CF@sub 2@ content. While some precursors, such as hexafluoropropylene oxide (HFPO), appear to deposit primarily in the off-time and is believed to be dominated by long-lived difluorocarbene species, other precursors, such as tetrafluoroethylene (TFE) show a linear dependence of deposition on duty cycle, suggesting deposition occurs primarily in the on-time period. To help elucidate the nature of the deposition processes and the differences between these precursors, UV absorption has been used to measure CF@sub 2@ concentrations quantitatively. In the plasmas examined here partial pressures of CF@sub 2@ are observed in the range of 5-15 mtorr for a 1 torr total pressure. Transients in concentration have been modelled by a elementary mole balance and effective reaction constants have been obtained. Optical emission spectroscopy and actinometry are also used to study the role of other species including O, F, CF and CF@sub 3@. XPS is used to study how the composition of the films varies with precursor and pulsing conditions, and can be related to the gas phase concentrations as measured by UV Absorption. Additionally, a quartz-crystal microbalance (QCM) has been used to measure deposition rates during the plasma on and off times.

Surface Science Division
Room 606 - Session SS1+EM-TuA
Oxides: Growth and Structure

Moderator: E.G. Seebauer, University of Illinois, Urbana

2:00pm **SS1+EM-TuA1 Noncommutative Band Offset at @alpha@-Cr@sub 2@O@sub 3@/@alpha@-Fe@sub 2@O@sub 3@(0001) Heterojunctions***, **S.A. Chambers**, Y. Liang,* Pacific Northwest National Laboratory

We have measured the valence band discontinuity at artificially structured, epitaxial heterojunctions of @alpha@-Cr@sub 2@O@sub 3@(0001) and @alpha@-Fe@sub 2@O@sub 3@(0001) grown on @alpha@-Al@sub 2@O@sub 3@(0001) substrates. Oxygen-plasma-assisted molecular beam epitaxy was the growth technique, and band offsets were measured by core-level and valence-band photoemission. Layered film structures of these two materials maintain the in-plane lattice parameter of @alpha@-Fe@sub 2@O@sub 3@(0001). Thus, the @alpha@-Cr@sub 2@O@sub 3@(0001) layers are under a 2.3% tensile stress. The valence band offsets

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

are 0.3±0.1 eV and 0.7±0.1 eV when the top layer is Fe@sub 2@O@sub 3@ and Cr@sub 2@O@sub 3@, respectively. The noncommutativity in band offset appears to be due to a growth-sequence-dependent interface dipole caused by different extents of intermixing for the two kinds of interfaces.

2:20pm **SS1+EM-TuA2 Ultrathin Iron Oxide Films***, **R.L. Stockbauer**, J. Karunamuni, A. Koveshnikov, R. Madjoe, R.L. Kurtz,* Louisiana State University

Thin films of spin polarized conductors are receiving increased attention as potential contacts for devices such as spin-valves and high-sensitivity disk sensors. We have succeeded in producing ultra thin films of FeO and Fe@sub 3@O@sub 4@ and characterized their morphology using STM and LEED. The oxides are grown by depositing thin films of Fe on a Cu(100) surface at room temperature. The Cu substrate has terraces ca. 100Å wide with steps perpendicular to the [010] direction. The Fe grows layer-by-layer in islands uniformly distributed on the Cu terraces. The oxides are formed by heating to 840K in 10@super -6@ Torr O@sub 2@. The change in the morphology of the surface after oxidation is truly striking. At low Fe coverage (<2ML), FeO completely rearranges the Cu substrate. Large terraces up to 1µm wide are now observed. The FeO itself forms long stripes typically 0.2µm wide and up to 10µm long parallel to the [011] direction. Shorter stripes are observed in the perpendicular direction. The FeO stripes display two superstructures. A coarse structure consists of a series of dark bands parallel to the stripe direction and spaced at 360Å intervals. The fine structure is a 20.5Å hexagonal pattern. A comparison of LEED data and simulations indicates that the overlayer is FeO(111) with stripes aligned along the [110] directions. Oxidizing Fe films thicker than 2ML results in the oxide phase of device interest, Fe@sub 3@O@sub 4@. These patches show a 170Å banded structure and the same size hexagonal superstructure but rotated 30° from that observed for the FeO . LEED data, simulations, and thermochemistry are consistent with the overlayer being Fe@sub 3@O@sub 4@(111) rotated 15° from the [001] azimuth. Surprisingly, these highly oriented oxide films do not show strong angular dependence in photoemission. MOKE, circular dichroism, and spin polarized measurements are underway to determine the magnetic properties of the oxide films.

2:40pm **SS1+EM-TuA3 Islanding, Facetting, and the Lattice Relaxation in the Growth of @alpha@-Fe@sub 2@O@sub 3@ on @alpha@-Al@sub 2@O@sub 3@***, **S.I. Yi**, Y. Liang, S. Thevuthasan, S.A. Chambers,* Pacific Northwest National Laboratory

The growth of @alpha@-Fe@sub 2@O@sub 3@ on c- and r-oriented @alpha@-Al@sub 2@O@sub 3@ by oxygen-plasma-enhanced molecular beam epitaxy has been investigated with reflection high-energy electron diffraction, non-contact atomic force microscopy, X-ray photoelectron spectroscopy, X-ray photoelectron diffraction, low-energy electron diffraction, and high-energy ion scattering. The epilayer is facetted due to compressional stress on the c-plane during growth of the first two monolayers. The epilayer structure is significantly distorted, with considerable in-plane strain. However, the film exhibits a constant Fe 2p binding energy with respect to the O 1s binding energy for all thicknesses, revealing the growth of phase-pure @alpha@-Fe@sub 2@O@sub 3@ throughout. A growth-mode transition begins at approximately two monolayers from strained wetting layer to the formation of clusters of rhombohedral islands when a relatively slow growth rate of 1 Å/min is used. However, this transition occurs over several monolayers at a growth temperature of 400 @super o@C. A film with high structural order and orientational stability grows as the islands coalesce to form new and larger terraces. This transition to island-mediated growth can be kinetically impeded for higher growth rates of 0.1-0.3 Å/sec.@footnote 1@ In contrast, the growth-mode transition will occur more rapidly if temperatures of 450 to 500 @super o@C are used along with the slower growth rate. However, sustained growth at temperatures in excess of 500 @super o@C results in the simultaneous formation of Fe@sub 3@O@sub 4@ (111) and/or @gamma@-Fe@sub 2@O@sub 3@ (111) along with @alpha@-Fe@sub 2@O@sub 3@(0001). In contrast to growth in the c-plane, the epilayer shows only facetted growth on the r-plane, regardless of the deposition rate and substrate temperature. This result may be due to the lower surface symmetry of the r-plane compared to the c-plane. @FootnoteText@ @footnote 1@ S. I. Yi, Y. Liang, S. A. Chambers, to be published in JVST A, Jul/Aug, 1999

3:00pm **SS1+EM-TuA4 Surface Reconstructions of Fe@sub 3@O@sub 4@(001)***, B. Stanka, W. Hebenstreit, **U. Diebold**,* Tulane University*; S.A. Chambers,* Pacific Northwest National Laboratory

We have investigated the structural changes to the Fe@sub 3@O@sub 4@(001) surface which are induced by different sample treatments. The samples consisted of ~5000 Å thick films of Fe@sub 3@O@sub 4@(001) , grown with oxygen-plasma-assisted molecular beam epitaxy (OPA-MBE) on MgO(001) substrates. To study the surface termination, structure, morphology, and composition, scanning tunneling microscopy (STM), low energy electron diffraction (LEED), low energy He@sup +@ ion scattering (ISS), and x-ray photoelectron spectroscopy (XPS) were used. A (@sr@(2) x @sr@(2))R45° reconstruction relative to bulk-terminated Fe@sub 3@O@sub 4@ is induced by heating in oxygen (10@sup -6@ - 10@sup -7@ mbar) at temperatures between 250°C and 500°C after a through-air transfer from the MBE chamber. Our STM results show an appearance consistent with a B-layer termination, which consists of a layer of octrahedrally coordinated Fe and tetrahedrally coordinated O, along with one O vacancy per unit cell. This surface is autocompensated, or charge neutral, and is therefore expected to be stable. Further annealing in UHV causes a transformation to either a (1 x n) or a (2@sr@(2) x @sr@(2))R45 structure. In both cases, a (@sr@(2) x @sr@(2))R45 reconstructed surface can be regained reproducibly by annealing in oxygen. Interestingly, at no time do we observe the other autocompensated termination, which consists of one-half monolayer of tetrahedrally coordinated Fe(III), despite its observation in other laboratories. Thus, it appears that the surface termination is critically dependent on the method of surface preparation.

3:20pm **SS1+EM-TuA5 The Surface Structure of @alpha@-Al@sub 2@O@sub 3@(0001) Studied by LEED***, **C.F. Walters**,* Sandia National Laboratories*; E.A. Soares, M.A. Van Hove,* Lawrence Berkeley National Laboratory*; K.F. McCarty,* Sandia National Laboratories

The surface structure of @alpha@-Al@sub 2@O@sub 3@(0001) has been investigated using normal-incidence low-energy electron diffraction. High quality sapphire samples were produced by ex-situ annealing in air, followed by in-situ cleaning using atomic deuterium at an elevated sample temperature. To investigate the possible occurrence of different surface structures and/or stoichiometries, the samples were processed, subsequent to the atomic deuterium cleaning, using several different procedures. These included annealing the sample in oxygen, and exposing the cooled sample to atomic deuterium. The experimental data were compared to results of calculations performed using an automated tensor LEED program. Several different models were used as the starting point for the analysis. These included termination by: an oxygen layer, a single aluminum layer, a double aluminum layer, and a "hydroxyl" covered single aluminum layer. Additionally, we have analyzed mixtures of these terminations, with the mixtures including different species, as well as the same species but containing different crystallographic planes (i.e., terraced surfaces with fractional unit cell step heights). For each sample preparation, the best structural model was determined via an analysis of the Pendry R-factor that took into account the effect of the additional fitting parameters for the models containing mixed terminations. The best-fit models derived from the tensor LEED analysis will be discussed with respect to the preparation method used, as well as compared to the results of recent first-principles calculations. This work supported by USDOE-OBES-Division of Materials Sciences.

3:40pm **SS1+EM-TuA6 Formation of Epitaxial Al@sub 2@O@sub 3@ on Ni@sub 3@Al(111) Studied by STM, HREELS, UPS, @DELTA@@PHI@, and LEED***, **A. Rosenhahn**, J. Schneider, J. Kandler, T. Pelster,* Universität Bonn, Germany*; R. Linke,* Eindhoven University of Technology, The Netherlands*; C. Becker, K. Wandelt,* Universität Bonn, Germany

The formation of oxides on the Ni@sub 3@Al(111) single crystal surface has been studied in the temperature range from 300K to 1000K by STM, HREELS, UPS, @DELTA@@PHI@, and LEED. The experiments reveal a strong temperature dependence of the structure and the chemical composition of the resulting oxides, which is caused mainly by a rising aluminum mobility with increasing temperature. Adsorption of oxygen at room temperature creates a disordered surface which appears rough in STM images and shows a diffuse LEED pattern. At 600K STM images show patches of different appearance on the alloy surface. At low coverages the small oxidic nuclei possess a triangular shape, and HREELS measurements show a Al@sub 2@O@sub 3@-like composition. At higher coverages two areas with different appearance can be distinguished in STM, accompanied by the observation of mixed Ni/Al-oxide vibrations in HREELS. At 800K STM measurements show highly ordered triangular shaped oxidic islands. A moiré structure can be observed which corresponds to a superstructure due to an unrotated single O/Al overlayer, that has also been found by LEED and HREELS measurements. The electronic structure of the film being very similar to that of O/Al(111). Adsorption at 1000K finally leads to the growth of an oxidic film, that proceeds from steps exclusively. The oxide exists in two rotational domains that can be detected in LEED and STM. Both HREELS and UPS measurements show the formation of a Al@sub 2@O@sub 3@-doublelayer. Only at this temperature the chemical order of the underlying Ni@sub 3@Al(111) substrate is completely restored.

4:00pm **SS1+EM-TuA7 Surface Structure Determination of Yttrium-Stabilized ZrO@sub 2@(001) Surface Using X-Ray Photoelectron Diffraction***, **S. Thevuthasan**, S.I. Yi,* Pacific Northwest National Laboratory*; Y.-J. Kim,* Taejon National University of Technology, Korea*; T.T. Tran, S.A. Chambers, C.H.F. Peden,* Pacific Northwest National Laboratory

The physical and chemical properties of oxide surfaces are strongly influenced by several structural properties. As such, there is a growing interest in determining surface termination and relaxation in single crystal oxides. The yttrium-stabilized ZrO@sub 2@(001) surface can in principle be either O terminated or Zr terminated. However, neither of these surfaces is autocompensated as a (1x1) structure. The Zr terminated @sr@2x@sr@2)R45@super o@ reconstruction is autocompensated. It was recently reported that the CeO@sub 2@(001)surface, which is similar to ZrO@sub 2@(001), is terminated with 0.5 monolayers of oxygen.@footnote 1@ We have carried out low-takeoff-angle x-ray photoelectron diffraction (XPD) measurements using Zr 3d, Y 3d and O1s core levels on a oxygen-plasma-cleaned ZrO@sub 2@(001) surface to determine the surface structure. Low-energy electron diffraction data show broad (1x1) spots that are characteristic of many oxide surfaces, and no half-order spots are visible. Currently single and multiple scattering simulations and R-factor analysis are being performed using model clusters generated using both O and Zr terminated surfaces. Preliminary analysis indicates that the surface is Zr terminated with the first layer spacing contracted by 23% relative to the bulk interlayer spacing. Detailed analysis is in progress and results will be presented at the meeting. @FootnoteText@ @footnote 1@G.S. Herman, Phys. Rev. B Rapid Comm. (in press). Work supported by the U.S. Department of Energy (DOE), Offices of Basic Energy Sciences, Division of Chemical Sciences and the DOE's Environmental Management Science Program.

4:20pm **SS1+EM-TuA8 Epitaxial Growth and Characterization of Zirconium-Doped CeO@sub 2@(111) Thin Films on Yttria-Stabilized Zirconia(111)***, **T.T. Tran**,* Pacific Northwest National Laboratory*; Y.-J. Kim,* Taejon National University of Technology, Korea*; S. Thevuthasan, G.S. Herman,* Pacific Northwest National Laboratory

Doping of the ceria lattice with Zr has been shown to enhance the oxygen storage capacity and the rate of oxygen release, and thus the catalytic properties of noble metals supported on these oxides.@footnote 1@ The ability to obtain a detailed knowledge of the effect of the surface structure and zirconium doping levels on oxygen exchange rates requires high-quality single crystalline materials. In a previous study, pure and Zr-doped CeO@sub 2@(001) thin films were grown on SrTiO@sub 3@(001).@footnote 2@ Due to the good lattice match and identical crystal structure, yttria-stabilized zirconia (YSZ) was chosen as the substrate for the growth of CeO@sub 2@(111) in this study. Both pure and Zr-doped CeO@sub 2@(111) thin films were grown on YSZ(111) by oxygen-plasma-assisted molecular beam epitaxy. After deposition, the films were compositionally and structurally characterized by in-situ reflection high-energy electron diffraction (RHEED), low-energy electron diffraction (LEED), x-ray photoelectron diffraction (XPD), and x-ray photoelectron spectroscopy (XPS), as well as by ex-situ Rutherford backscattering spectrometry. RHEED, LEED, and XPD results indicated that the materials are well-ordered at the surface for zirconium doping levels up to 40%. Furthermore, a +4 oxidation state was confirmed for both Zr and Ce using XPS. RBS results showed that Zr was found to incorporate substitutionally at cation sites in the ceria lattice. @FootnoteText@ @footnote 1@ P. Fornasiero, G. Balducci, J. Kaspar, S. Meriani, R. Di Monte, and M. Graziani, Catal. Today, 29, 47 (1996); Hamada, H., Catal. Today, 22, 21 (1994); Ozawa, M., M. Kimura, and A. Isogali, J. Alloys Comp., 193, 73 (1993). @footnote 2@ Y. Gao, G.S. Herman, S. Thevuthasan, C.H.F. Peden, and S.A. Chambers, J. Vac. Sci. Technol. (in press).

4:40pm **SS1+EM-TuA9 Structure and Dynamics of KTaO@sub 3@(001) via Elastic and Inelastic Helium Atom Scattering@footnote 1@***, J.A. Li, T.W. Trelenberg, E.A. Akhadov, S.A. Safron, **J.G. Skofronick**,* Florida State University*; L.A. Boatner,* Oak Ridge National Laboratory

Although bulk KTaO@sub 3@ is considered an incipient ferroelectric which remains cubic at all temperatures, He diffraction on the (001) surface, cleaved in situ, shows reconstruction of the (1x1) surface to (2x1). The surface behavior, however, seems to depend on its thermal history as, for example, in the following observations: 1)After the sample is cleaved at about 300K and cooled to about 190K, He diffraction reveals a (1x1) surface which appears to be stable indefinitely. 2)If the target is then warmed from 190K to about 220K, reconstruction to the (2x1) phase takes place gradually over a period of about 2 days, whereas if it is warmed to about 260K, the (2x1) phase becomes evident after about 3 hours. 3)When the target is instead taken from 190K to approximately 60K and then to about 260K, the (2x1) surface is apparent immediately. 4)Restoration to (1x1) can be achieved (a) in a few hours or (b) immediately by warming the surface to about 330K or to about 360K, respectively. In addition, there is considerable hysteresis in the intensities of the He diffraction spots for the (2x1) surface over the thermal cycle from 260 K to 50 K to 260 K. Helium time-of-flight (TOF) spectra were obtained to determine the surface phonon dispersions of the (1x1) and (2x1) surfaces for several surface temperatures between 80K and 300K. These appear very similar over the entire surface Brillouin zone. The dominant peaks in the TOF spectra correspond to a dispersionless mode at about 13.5meV, which stiffens slightly as the temperature is raised. However, the lowest energy branch which is quite flat at low temperatures seems to soften near the zone center as the temperature increases. @FootnoteText@ @footnote 1@Supported by U. S. Department of Energy grant number DE-FG02-97ER45635.

5:00pm **SS1+EM-TuA10 Deposition of Highly Oriented Mg@sub 3@(VO@sub 4@)@sub 2@ Thin Films for Use in Catalysis Studies***, **J.A. Ruffner**, A.G. Sault,* Sandia National Laboratories

Magnesium vanadates are potentially important catalytic materials for the conversion of alkanes to alkenes via oxidative dehydrogenation. However, little is known about the active sites at which the catalytic reactions take place. It may be possible to obtain a significant increase in the catalytic efficiency if the effects of certain material properties on the surface reactions could be quantified and optimized through the use of appropriate preparation techniques. Given that surface reactivity is often dependent upon surface structure and that the atomic level structure of the active sites in these catalysts is virtually unknown, we desire thin film samples consisting of a single magnesium vanadate phase and a well defined crystallographic orientation in order to reduce complexity and simplify the study of active sites. We report on the use of reactive RF sputter deposition to fabricate very highly oriented, stoichiometric Mg@sub 3@(VO@sub 4@)@sub 2@ thin films for use in these surface analysis studies. Preliminary depositions of Mg@sub 3@(VO@sub 4@)@sub 2@ onto amorphous substrates resulted in amorphous thin films. However, deposition of Mg@sub 3@(VO@sub 4@)@sub 2@ onto well-oriented, lattice-matched thin film "seed" layers such as Ti (0002), Au (111) or Pt (111) resulted in very strong preferential (042) crystallographic orientation (pseudo-hexagonal planes parallel to the substrate). This strong preferential growth of the Mg@sub 3@(VO@sub 4@)@sub 2@ suggests epitaxial (single-crystal) growth of this mixed metal oxide on the underlying metal seed layer. The effects of the substrate material, seed layer material, deposition temperature, and post-deposition anneal temperatures on thin film properties such as stoichiometry, crystallographic orientation, and chemical interactions will be reported.

Surface Science Division
Room 6C - Session SS2+EM-TuA

Semiconductor Surface Chemistry

Moderator: R.M. Feenstra, Carnegie Mellon University

2:00pm **SS2+EM-TuA1 Medard W. Welch Award Address: Halogen Etching of Si with Emphasis on Atomic-Scale Processes***, **J.H. Weaver**[1],* University of Minnesota **INVITED**

Etching is the process of producing a pattern on a surface, and it is central to a great many technologies. Indeed, etching (material removal) plays a complementary role to growth (material addition), and product fabrication

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[1] **Medard W. Welch Award Winner**

includes both etching and growth. This talk will review recent progress made in understanding surface etching of semiconductors. Emphasis will be on atomic-scale changes in surface morphologies for Si(100) etched with halogens, where the parameters that are controlled are the flux and the fluence of the beam and the reaction temperature of the substrate. The kinds of information that can be gained from atomic-resolution scanning tunneling microscopy will be highlighted. Etch morphologies will be linked to site-specific desorption energies, with consideration of terrace pitting and the formation of nanometer-scale patterns. The sequence of events leading to dihalide desorption and the role of vacancies will be described. Comparison of results for F-Si(100) and Cl-Si(100) shows the formation of defects in the second layer for F, a process that results in roughening rather than layer-by-layer etching observed for Cl.

2:40pm **SS2+EM-TuA3 Micrometer-scale "Grooves" and Step Bunching during Extended Oxidation-induced Etching of Si(001) Surfaces***, **J.F. Nielsen**,* The Ohio State University*; M.S. Pettersen,* Otterbein College*; J.P. Pelz,* The Ohio State University

We have used in-situ STM and ex-situ AFM to observe large-scale step rearrangement on Si(001) surfaces that were heated by DC current at ~1000@super o@C for 3-43 hrs in ~10@super -5@ Torr of oxygen. Depending on sample miscut and current direction, these conditions produced either (1) no significant step rearrangement, (2) large scale (5-10µm) step-bunched regions (with separation increasing roughly as t@super 1/2@), or (3) large "grooves", consisting of a highly-ordered sinusoidal step array with in-phase alignment. The grooved and step-bunched phases can coexist on the same wafer, forming neighboring semi-coherent patches extending over hundreds of microns. The interface between the two phases is remarkably sharp. The step-bunching was also observed on surfaces heated in vacuum (no oxygen), and may be similar to electromigration-related behavior reported by Doi et al.@footnote 1@ Regular arrays of "crossing steps" are also seen on the step bunched regions. It is not yet clear whether oxygen is required for the formation of the grooves. The grooves appear to be qualitatively different from the "wavy" steps reported by Tromp and Reuter@footnote 2@ in that they extend coherently over large areas and are not confined to sample regions of extremely low-miscut. We are currently mapping out the precise conditions necessary to produce each surface phase, and are using the wide terraces resulting from step-bunching in on-going studies of spontaneous step creation on ultra-flat Si(001) surfaces. @FootnoteText@ @footnote 1@ T. Doi, M. Ichikawa, and S. Hosoki, Phys. Rev. B. 55, 1864 (1997) @footnote 2@ R. M. Tromp and M. C. Reuter, Phys. Rev. Lett. 68, 820 (1992).

3:00pm **SS2+EM-TuA4 The Structure of Steps on Hydrogen-Passivated Si Surfaces***, **A. Laracuente**, L.J. Whitman,* Naval Research Laboratory

Steps play a critical role during epitaxy, so knowing their structure is crucially important to understanding how films grow. There has been a considerable effort to determine the step structure on Si surfaces oriented near (001).@footnote 1@ On surfaces tilted toward (111), there are four distinct step configurations, single- and double-layer A-type and B-type steps, commonly denoted as S@sub A@, S@sub B@, D@sub A@, and D@sub B@. B-type steps are almost always "rebonded," with two extra atoms per unit cell at the step edge. The extra atoms halve the dangling bond density along each step and thereby make this structure energetically preferred over a non-rebonded configuration. On surfaces tilted more than 3°, only rebonded D@sub B@ steps occur. Because most industrial Si film growth happens in the presence of hydrogen, an accurate picture of such growth requires an understanding of how H affects the Si step structure and dynamics. It was recently predicted theoretically that non-rebonded steps should be energetically more favorable on H-terminated Si.@footnote 2@ We have now verified this prediction experimentally on a range of surfaces oriented from (001) to (114). We find that S@sub B@ steps "unrebond" after H-passivation, as predicted, completely altering the step energetics. Similarly, H passivation splits a large fraction of D@sub B@ steps into S@sub A@+S@sub B@ step combinations. These changes in step structure have a dramatic effect on the step dynamics and the resulting surface morphology, generally leading to much rougher surfaces. We will discuss how these changes can explain a variety of previous observations about the effects of H on Si film growth. @FootnoteText@ @footnote 1@ A. A. Baski, S. C. Erwin, and L. J. Whitman, Surf. Sci. 392, 69 (1997). @footnote 2@ S. Jeong and A. Oshiyama, Phys. Rev. Lett. 81, 5366 (1998).

3:20pm **SS2+EM-TuA5 Microscopy of Si(001) Surface Defects Produced by keV He Ion Irradiation at Low Temperatures***, K. Kyuno, **D.G. Cahill**, R.S. Averback,* University of Illinois, Urbana-Champaign*; J. Tarus, K. Nordlund,* University of Helsinki, Finland

The interactions of bulk point defects (interstitials and vacancies) with silicon surfaces influences microstructures and dopant profiles created by low-energy ion implantation. To gain insight on the migration of ion-induced defects and their interactions with surfaces, we use variable temperature scanning tunneling microscopy (STM) to measure the areal density of surface defects created by 5 keV He ion irradiation of Si(001) at low temperatures. Samples are irradiated to a dose of 1.7 and 3.4x10@super 13@ ions cm@super -2@ at 80, 130, 180, and 294 K, and imaged at the same temperature. Because of the background density of surface vacancies, we focus our analysis of the STM images on the densities of adatoms, dimers, and clusters formed by the ion bombardment. The density of these protrusions at 80 and 130 K is approximately linear in dose, independent of temperature, and in reasonable agreement with our molecular dynamics calculations of surface defect concentrations. At 180 K, the measured density of protrusions is enhanced by a factor of ~3; we interpret this result in terms of the onset of bulk defect migration. Surprisingly, the Si(001) surface appears to be a relatively inefficient trap for bulk defects under our experimental conditions; our results can be explained by the migration and trapping of defects formed within less than 1 nm of the surface.

3:40pm **SS2+EM-TuA6 A Variable Temperature Scanning Tunnelling Microscopy Study of Si(100) Etching Dynamics***, **C.F. Herrmann**, J.J. Boland,* University of North Carolina

The etching behavior of bromine on the Si(100) surface was investigated using variable temperature scanning tunneling microscopy (VT-STM). The clean Si(100) was initially dosed with bromine to passivate the surface. The passivated surface was then heated slowly and imaged simultaneously with no additional bromine exposure. STM images were taken at several temperatures from 600K to 750K to study the etching dynamics of Si(100) with bromine. The initial distribution of vacancies peaked at a single dimer unit and decayed monotonically to higher lengths. After further heating, repartitioning was observed and dimer vacancies of odd lengths were preferentially formed. The motion of single dimer vacancies was also observed in addition to a novel etching structure. The implications for chemical etching are discussed.

4:00pm **SS2+EM-TuA7 Dissociative Adsorption and Recombinative Desorption of H2 on Si(100)-2x1***, **F.M. Zimmermann**, X. Pan,* Rutgers University

The interaction of hydrogen with Si(100) is of considerable technological importance since hydrogen desorption is the rate-limiting step in low-temperature chemical vapor deposition of Si. Furthermore, this system is intriguing from a fundamental point of view, due to a multitude of unusual and remarkable experimental observations, such as desorption kinetics intermediate between first order and second order, and the so-called 'barrier puzzle': A large barrier to adsorption is seen in adsorption experiments, whereas in desorption dynamics experiments the desorbing molecules paradoxically show no signs of having traversed such a barrier. Using surface second harmonic generation, we have measured the adsorption and desorption kinetics as a function of surface temperature, H coverage, and exposure pressure. These measurements reveal more highly unusual kinetic behavior. Contrary to what is expected from Langmuirian site-blocking considerations, the sticking probability increases markedly with coverage, indicating a self-catalyzed adsorption mechanism. In addition, the sticking probability exhibits a pronounced dependence on exposure pressure, ruling out most 'simple' adsorption mechanisms. The observations are interpreted in terms of a self-catalyzed, barrier-less, inter-dimer adsorption mechanism (observed with the STM by Biedermann, Knoesel, Hu, and Heinz, submitted to Phys. Rev.). Our model quantitatively explains the measured adsorption and desorption kinetics (temperature, coverage, and pressure dependence), and provides a natural explanation of the vexing barrier puzzle. Fitted model parameters are in very good agreement with independently obtained experimental and theoretical values.

4:20pm **SS2+EM-TuA8 Novel Mechanisms for Plasma Etch Front and CVD (Chemical Vapor Deposition) Growth Front Roughening***, **Y.-P. Zhao**[1], J.T. Drotar, G.-C. Wang, T.-M. Lu,* Rensselaer Polytechnic Institute

Plasma etching and chemical vapor deposition (CVD) are major tools for thin film processing in microelectronic industry. Although kinetic roughening of thin films has attracted considerable attention in recent years, very little work has been focused on the study of surface roughening mechanisms during plasma etching and chemical vapor deposition. Here, we report a novel etch front roughening phenomenon during the plasma etching of Si(100) substrates. The surface power spectrum shows an obvious wavelength selection which does not occur in conventional noise-induced roughening. The average local surface slope is almost invariant while the vertical roughness grows as a power law in time, w ~ t^@beta@, with a growth exponent @beta@ = 0.91 ± 0.03. We develop a general non-local model to describe the roughening process in plasma etching based on the gas transport kinetics for a large Knudsen number. The flux of the reactive particles redistributes according to the re-emission mechanisms that are influenced by the surrounding morphology. Our extensive numerical calculations and Monte Carlo simulations for various re-emission modes show that @alpha@ (roughness exponent) ~ @beta@ ~ z ~ 1 for plasma etching, which is consistent with our experimental results. Our calculations demonstrate that the proposed model is universal in describing the roughening of plasma etching. In addition, the reverse of this model can be used to describe CVD growth. Our Monte Carlo simulations show that @alpha@ ~ @beta@ ~ 0, z ~ 2 for CVD growth. Detailed comparisons between local and non-local dynamic growth models, as well as the growth and etching processes will also be presented. @FootnoteText@ Work supported by NSF.

4:40pm **SS2+EM-TuA9 Resonance-Enhanced Multiphoton Ionization Studies of the Etching of Silicon by Molecular Chlorine***, **T.A. Barckholtz**, L. McDonough, S.R. Leone,* University of Colorado, Boulder

Laser ionization time-of-flight mass spectrometry is a powerful technique for characterizing the neutral products of the etching of semiconductor materials. We previously showed that single photon ionization (SPI), which uses the 9th harmonic of a Nd:YAG laser, provides excellent characterization of the neutral products of the etching of silicon by molecular chlorine, both thermally@footnote 1@ and during ion-enhanced etching.@footnote 2@ Two drawbacks of using the SPI technique are the low laser power available (ca. 10 µJ/pulse) and the lack of resolution of the state distributions (electronic, vibrational, rotational) of the products. To address these deficiencies, we recently implemented a Nd:YAG-pumped dye laser on an etching apparatus that enables resonant electronic multiphoton ionization (REMPI) schemes for the detection of the neutral species. Because of the greater laser power available (several mJ/pulse), the detection sensitivity has been dramatically increased. For example, the REMPI signal intensity of neutral atomic Si during thermal etching is approximately 200 times greater than the SPI intensity. Furthermore, complete state resolution of the Si spin-orbit (@super 3@P@sub 2@, @super 3@P@sub 1@, and @super 3@P@sub 0@) and metastable (@super 1@D@sub 2@) states is obtained. For SiCl, due to its broad rotational and vibrational distributions, the detection sensitivity is increased by a smaller factor, and only partially resolved state distributions are possible. We plan to use the enhanced sensitivity and partial state resolution to investigate the mechanism for the ion-enhanced etching of silicon by chlorine in greater detail than was possible with the SPI technique. The results of these studies will be compared with the predictions of published molecular dynamics simulations. @FootnoteText@ @footnote 1@Materer, N.; Goodman, R. S.; Leone, S. R. JVST A 1997, 15, 2134-2142. @footnote 2@Goodman, R. S.; Materer, N.; Leone, S. R. JVST A, submitted for publication.

5:00pm **SS2+EM-TuA10 Femtosecond Photo-induced Dynamics on a Cleaned and a Chlorinated Si(111) Surfaces***, **S. Haraichi**, F. Sasaki,* Electrotechnical Laboratory, Japan

A photo-induced chemical etching of Si is considered as a powerful candidate of the next-generation device fabrication thechnology from the view point of extremely low damage. However the atomic and/or dynamic mechanisms of the photo-induced reaction of Si/halogen systems have not been well understood. We have investigated photo-induced dynamics on a cleaned and a chlorinated Si(111) surfaces using femtosecond second-harmonic generation (SHG). For the pump-probe measurements, Ti-sapphire laser at 1300nm and 800nm with a 100fs pulse width were used as the probe and the pump beams, respectively. With the wavelength at 1300nm, a contribution of absorption is negligible and the surface specific information can be obtained. SHG intensities from a cleaned 7x7 surface decay rapidly just after the pump beam coincides with the probe beam and increase with a rapid and a slow time constants of around 1ps and more than several tens ps. These results were probably due to an immediate photo-excitation and two kinds of relaxation of 7x7 surface states. On the other hand, SHG intensities from a chlorinated Si surface increase rapidly just after the pump beam irradiation and decay with a time constant of around several ps, based on Si-Cl bonding states. On both a cleaned and a chlorinated Si surfaces, the time constants show no significant dependence on the pump beam fluency under the critical fluency of the etching reaction.

Surface Science Division
Room 607 - Session SS3-TuA
Diffusion on Surfaces

Moderator: T.L. Einstein, University of Maryland

2:00pm **SS3-TuA1 Mechanisms and Energetics in Diffusion of O2-Molecules and H-atoms on Si(1x1)-7x7 Surfaces***, **R.L. Lo**, I.S. Hwang, M.S. Ho,* Academia Sinica, Republic of China

Using a variable temperature STM, atom and molecular dynamics on solid surfaces can be observed directly and the energetics studied in detail. It is possible to trace the path of single particle movement, measure site and path specific hopping rates and the rate parameters of individual atoms and molecules on solid surfaces as well as to probe the mechanisms. We find that on Si(111)-7x7 surface, O2 molecules adsorb on top of adatom sites while H atoms adsorb on top of rest atom sites. Diffusion and hopping of H and O2 on this surface is achieved by hopping of chemical bonds via intermediate states. We have identified the intermediate states and also derived site and path specific activation energies and frequency factors, and the potential energy curves for the hopping of O2 and H on this surface. The physical significance of these measurements will be discussed. Research supported by NSC of ROC and Academia Sinica. 1. I-S Hwang, R-L Lo and T. T. Tsong, Phys. Rev. Lett. 78, 4797 (1997). 2. R-L Lo, I-S Hwang, M-S Ho and T. T. Tsong, Phys. Rev. Lett. 80, 5584 (1998).

2:20pm **SS3-TuA2 Real-Time Imaging of Step Motion on Cu(100) with the Low Energy Electron Microscope@footnote 1@***, **C.L.H. Devlin**, S. Chiang, X.D. Zhu,* University of California, Davis

The low energy electron microscope (LEEM) is capable of real-time, real-space imaging of metal and semiconductor surfaces, at the scale of tens of nanometers. We have recently used a new instrument at UC Davis to image the motion of steps on the Cu(100) surface. We have seen a number of intriguing effects at the relatively low temperature range of 100 to 300°C. Impurities pin the step positions, affecting the shapes of the steps over regions of many microns. The kink density of the steps decreases with additional sample cleaning, with the steps becoming more rectilinear. Evidence exists for several different phases on the surface as a function of temperature, as the contrast on terraces changes markedly on the scale of 10-20 nm with increasing temperature. The size of an area corresponding to a particular phase also changes. In some cases, rapid fluctuations of the contrast at the boundaries are evident as the phase shrinks. For curved steps, wave-like motions have been observed along the length of steps. Steps have also been observed to move into and out of an impurity at constant temperature. An X-ray photoemission spectrometer and a commercial variable temperature scanning microscope (VT-STM) (50-800K) have recently been added to the UC Davis LEEM system and are being used to further characterize the Cu(100) system. @FootnoteText@ @footnote 1@Funded by National Science Foundation (DMR-95-12231) .

2:40pm **SS3-TuA3 Diffusion and Dynamics of 2D Clusters on Crystal Surfaces***, G. Rosenfeld,* University of Twente, The Netherlands*; **L.K. Verheij**, D.C. Schloesser,* IGV, Forschungszentrum Jülich, Germany*; G. Comsa,* University of Bonn, Germany **INVITED**

Using fast scanning tunneling microscopy, the diffusion and shape fluctuation of nanoscale vacancy clusters on a Cu(111) surface have been studied. The diffusion constant has been determined as a function of cluster size and temperature, and the underlying atomic scale diffusion processes have been deduced.@footnote 1@ The results are discussed with respect to simple scaling theories. Via detailed analysis of cluster shapes and shape fluctuations both the anisotropy and the absolute value of the line tension, i.e., the specific free energy of cluster edges, have been determined.@footnote 2@ The experimental data yield a comprehensive

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

set of energies believed to be representative for the diffusion and stability of 2D metal clusters on fcc(111) surfaces. @FootnoteText@ @footnote 1@ D.C. Schloesser, L.K. Verheij, G. Rosenfeld, G. Comsa, to be published @footnote 2@ D.C. Schloesser, L.K. Verheij, G. Rosenfeld, G. Comsa, Phys. Rev. Lett. 82, 3843 (1999).

3:20pm **SS3-TuA5 Sulfur's Effect on Cu(111) Surface Morphology***, **J. de la Figuera**, K. Pohl, M.C. Bartelt, N.C. Bartelt, P.J. Feibelman, R.Q. Hwang,* Sandia National Laboratories

Numerous studies have demonstrated the dramatic effects that small amounts of an adsorbate can have on film growth and surface morphology. The origin for these effects range from kinetic limitations to thermodynamic considerations. We have recently observed that extremely small amounts of sulfur can significantly affect the smoothing of Cu(111). Cu islands of monolayer height decay several orders of magnitude faster in the presence of ~0.01 ML of sulfur as compared to the clean case. Using time-resolved STM, we have monitored the rate and morphology of the decay to identify the origin of this phenomenon. In agreement with these observations, first-principles calculations predict a dramatic change in the ratio of Cu step formation energies in the presence of a row of S atoms at the steps. Sulfur atoms bind more strongly to the A-type step. The ratio of the equilibrium lengths of the A- and B-type steps is about 1:1.1 on the clean surface, but about 2.4:1 when the step edges are S-saturated. We discuss the observed superfast island decay in terms of atomic processes at and near island edges, including S-mediated near-irreversible detachment of Cu atoms, enhanced diffusion of Cu adatoms and small clusters on the terraces, and more efficient downward transport. This work is supported by the Office of Basic Energy Sciences Division of Materials Sciences of the U.S. DOE (DE-AC04-94AL85000).

3:40pm **SS3-TuA6 Influence of Adsorbates on the Self-diffusion of Pt Adatoms and the Stability of Pt Dimers***, **S. Horch,*** University of Aarhus, Denmark*; T.R. Linderoth,* University of Aarhus, Denmark, Sweden*; S. Helveg, L. Petersen, E. Laegsgaard, I. Stensgaard, F. Besenbacher,* University of Aarhus, Denmark

Surface diffusion of atoms is an important phenomenon in areas of materials processing such as chemical vapor deposition (CVD) and sintering. In these particular areas, the diffusion are modified by atoms adsorbed from the gas phase. Here we try to derive mechanistic insight into this effect from observations, using the Scanning Tunneling Microscope, of adsorbate promoted self-diffusion on the Pt(110)-(1x2) surface.@footnote 1@ In the case of hydrogen, we directly image an activated Pt-H complex (with H bound on top the Pt adatom) which has a diffusivity enhanced by a factor of 500 at room temperature, relative to Pt adatoms on the clean surface. The influence of other adsorbates also on the binding energy of Pt dimers is currently being investigated. @FootnoteText@ @footnote 1@ S. Horch, H. T. Lorensen, S. Helveg, E. Laegsgaard, I. Stensgaard, K. W. Jacobsen, J. K. Norskov and F. Besenbacher, Nature 398 (1999) 134.

4:00pm **SS3-TuA7 Study of Subsurface Hydrogen in Pd(111) by STM***, **M.K. Rose**,* Lawrence Berkeley National Laboratory*; A. Borg,* Norwegian University of Science and Technology, Norway*; D.F. Ogletree, M. Salmeron,* Lawrence Berkeley National Laboratory

Using Variable Temperature Scanning Tunneling Microscopy we have studied hydrogen atoms embedded in the topmost layers of Pd(111) and the influence of these impurities on surface adsorbates. Hydrogen is imaged beneath surface three-fold hollow sites at 20K. Subsurface hydrogen atoms exhibit attractive interactions leading to aggregation into clusters. We observe diffusion of two distinct hydrogen species within the subsurface layer above 200K, with activation energies differing by approximately 10%. Significant variation in the diffusion barriers is found in the presence of surface adsorbates. Interlayer diffusion is not observed below 220K, which sets lower bounds on the surfacesubsurface and subsurface-bulk diffusion barriers and provides a benchmark for ab-initio total energy calculations. Scanning Tunneling Spectroscopy of subsurface hydrogen has been performed and the results are compared with tight-binding calculations. Adsorbed molecules interact strongly with subsurface H. In the case of CO, binding occurs preferentially at sites separated by @sr@3 lattice vectors from surface hollow sites above embedded hydrogen. For O@sub 2@, thermal dissociation proceeds adjacent to H sites. Subsurface H clusters provide nucleation sites for ordered adsorbate structures, pin adsorbate domain boundaries, and hinder adsorbate diffusion.

4:20pm **SS3-TuA8 Enhanced Interlayer Mass Transport and Dynamics of Film Smoothening on a Symmetry-broken Ag(111) Surface***, **H. Yu**, C.-S. Jiang,* University of Texas, Austin*; Ph. Ebert,* Forschungszentrum J@um u@lich, Germany*; X.-D. Wang, C.K. Shih,* University of Texas, Austin

We have studied the dynamics of the film flattening process at room temperature and higher annealing temperatures of Ag films deposited at low temperature on GaAs(110) surfaces. We will present a scanning tunneling microscopy movie, which shows the evolution of the film morphology over 13 hours at room temperature. The initial surface contains a distribution of surface heights up to five monolayers. The vacancy islands at the lowest layer and the islands at the top layer both decay very rapidly with the same decay constants. The remaining islands (of a surface with three monolayers exposed) decay with a much slower rate and we observed a freeze of decay after about 7 hours. Consecutive annealing up to 400 K induces a further decay of the roughness, such that finally nearly only two layers are exposed. The island size increased during room temperature and consecutive annealing steps considerably and the steps align preferentially along the high symmetry directions of the twofold superstructure present on the Ag surface. These results demonstrate the existence of a considerably enhanced interlayer mass transport and a different symmetry behavior compared to those observed for Ag homoepitaxy on Ag(111) surfaces. The enhanced interlayer mass transfer is interpreted in terms of a very low Ehrlich-Schwoebel barrier.

4:40pm **SS3-TuA9 Ion-Enhanced Surface Diffusion: Experiment and Simulation***, **E.R. Blomiley**, Z. Wang, E.G. Seebauer,* University of Illinois, Urbana

Low-energy ion enhancement of thin film deposition has become an increasingly widespread technique for lowering growth temperatures and improving film properties. Rational process optimization has remained difficult, however, because the beneficial effects of enhanced surface diffusion are often opposed by the deleterious effects of sputtering and ion embedding. Good explanations for important aspects of the governing physical processes remain lacking. We have recently reported for the first time direct quantitative measurements of low-energy (<70 eV) ion-enhanced diffusion, using the Ge/Si(111) adsorption system with noble gas ions as the bombarding species. The present work extends that work to examine the effects of incident bombardment angle. Experiments with second harmonic microscopy show that below about 750°C, diffusional enhancement increases monotonically as the incident angle increases from normal toward grazing. However, above 750°C diffusional effects change nonmonotonically in a manner more akin to sputtering yields. Molecular dynamics simulations show these effects arise from ion-induced adatom-vacancy pair formation.

5:00pm **SS3-TuA10 The Effect of As@sub 4@ Flux on the Ga Diffusion on the GaAs(001)-(2x4) Surface***, **D.W. Bullock**, V.P. LaBella, Z. Ding, P.M. Thibado,* University of Arkansas

The activation energy for an individual Ga atom to hop across the technologically important GaAs(001) 2x4 reconstructed surface as a function of As@sub 4@ flux was measured. This study was motivated by the ongoing development of short-period III-V semiconductor superlattices for electronic and optoelectronic applications grown by molecular beam epitaxy (MBE). This study was carried out in an ultrahigh vacuum MBE system with an in situ scanning tunneling microscope (STM) to study III-V single cryst al surfaces and interfaces on the atomic scale. The diffusion measurement was achieved by measuring the number density of islands as a function of substrate temperature and As@sub 4@ flux, and comparing it to random walk computer simulations of the grow th process. The Ga atom's relative probability to stick to existing island edges and its relative diffusion anisotropy are estimated. Interestingly, it was discovered that increasing the As@sub 4@ pressure forces the Ga atoms to diffuse more isotropically. This work was funded in part by the National Science Foundation (DMR-9733994) and the Office of Naval Research (N00014-97-1-1058).

Thin Films Division
Room 615 - Session TF-TuA
Fundamentals of Si and Dielectric PVD

Moderator: S. Zarrabian, Optical Coating Labs

2:00pm **TF-TuA1 Preparation of Co and CoN@sub x@ Thin Films by Unbalanced r.f. Magnetron Sputtering**, ***T. Tanaka,*** Hiroshima Institute of Technology, Japan; *A. Kitabatake,* Sanyo Shinku Kogyo, Japan; *K. Kawabata,* Hiroshima Institute of Technology, Japan

It has been difficult to deposit ferromagnetic thin films by using a conventional planar magnetron sputtering at low pressure. We have developed a modified process based on an unbalanced magnetron sputtering of a magnetic Co target (100 mm, 5mm thick) to deposit Co and CoN@sub x@ films where an external magnet is added to a conventional planar magnetron to confine the efficient plasma near the magnetron target. The plasma confinement can be controlled by the shape of the magnetic field in the sputter deposition device with a multipolar magnetic-field plasma confinement. Cobalt films were prepared by this sputtering system at the r.f. powers of 100 to 200 W and argon pressure less than 5x10@super -3@ Torr. It is shown that the deposition rate of Co films significantly increases from 8.7 to 25 nm/min whose values are two times that of a conventional magnetron sputtering. Co film with the preferred orientation of (111) plane is formed and the value of the grain size estimated from the plane is about 30 nm. Cobalt nitride (CoN@sub x@) films were also prepared by the unbalanced magnetron sputtering in mixtured argon and nitrogen plasma. It is also found from the results of electron probe microanalysis that the content of nitrogen in CoN@sub x@ films increases with the increasing gas flow ratio of N@sub 2@ . The electrical resistivity for reactively sputtered films is less than 80x10@super -6@ @ohm@ cm which makes this compound a relatively good conductor.

2:20pm **TF-TuA2 Microstructural Control of Thin Silicon Films Grown by Reactive Magnetron Sputtering Utilizing Low Energy Ion Bombardment**, ***J. Gerbi,*** *J.R. Abelson,* University of Illinois, Urbana-Champaign

We use spectroscopic ellipsometry, Raman scattering, TEM, SIMS, and photoluminescence to analyze the optical properties and microstructure of hydrogenated or deuterated Si thin films of various crystallinities. Bulk mc-Si films are of current interest for solar cell, hybrid solar cell, and thin film transistor applications; low temperature deposition enables the use of plastic substrates. We have previously demonstrated that RMS can deposit mc-Si films directly on glass with no amorphous boundary layer,@footnote1@ and that substituting D2 for H2 in the growth process enhances crystallinity.@footnote2@ In this work, we deposit 0.5 micron thick hydrogenated or deuterated mc-Si films on glass substrates by RMS of a Si target using 1.6 mT Ar plus H2 or D2 at partial pressures from 0 mT (producing amorphous films) to 5.5 mT (producing fully microcrystalline films) at substrate temperatures of 120 and 230 C. In our system, the ion flux and energy are decoupled parameters. The ion flux is controlled by the application of a cylindrical magnetic field created by external coils. This field directs a weak plasma toward or away from the substrate, controlling the ion flux such that the ratio of arriving ions to depositing Si atoms can be varied from < 1 to > 30. The ion energy is also externally controlled by biasing the substrate. We find marked differences in microstructure using high ions fluxes at energies <~ 30 eV, and we will report both the microstructural and optical properties of the films. We also show that biasing of the substrate to produce ion energies >= 50 eV (as often done in conventional diode sputtering systems at higher pressures) produces damage which degrades the mc-Si microstructure. @FootnoteText@ @footnote 1@Y. H. Yang and John R. Abelson, Appl. Phys. Lett. 67, 3623 (1995). @footnote 2@ J. E. Gerbi and John R. Abelson, "Enhanced Crystallinity of Microcrystalline Silicon using Deuterium in Low Temperature Reactive Magnetron Sputter Deposition," MRS Proc. 507, 429 (1998).

2:40pm **TF-TuA3 PVD of Thin Film Silicon: How Fast Light Atom and Slow Heavy Ion Bombardment During Growth Promote Low-Temperature Crystallinity**, ***J.R. Abelson,*** University of Illinois, Urbana **INVITED**

Macro-electronic devices such as photovoltaic cells and active matrix displays are based on the deposition of thin semiconductor films onto large area substrates at low temperatures. Silicon presents an interesting case because the microstructure can range from amorphous to nanocrystalline to polycrystalline. These different microstructures can be produced by manipulating the concurrent particle bombardment during PVD growth by dc reactive magnetron sputtering of a Si target in Ar + H2. Three types of particles impinge on the film: (i) sputtered Si atoms of a few eV; (ii) H atoms with ~ 100 eV, generated by the acceleration and reflection of H2+ ions at the target; and (iii) bulk plasma Ar+ and H2+ ions with ~ 25 eV, whose flux is controlled using an externally-generated magnetic field to unbalance the magnetron. We analyze the growth process using real-time mass spectroscopy, spectroscopic ellipsometry, and reflection IR absorption, including isotopic H2/D2 exchange experiments. We combine these data with binary collision simulations in the gas-phase and substrate to show how each flux modifies the microstructure. The essential results are: (i) Few-eV sputtered Si atoms produce a dense microstructure, as predicted by the Thornton zone diagram, but also lead to the random formation of nanocrystalline Si particles in an amorphous Si matrix. These particles can serve as nuclei for solid-phase crystallization processes. (ii) 100 eV H atoms penetrate ~ 50 A into the growing film, where they drive crystalline nucleation and subsurface transformation through bond-insertion and momentum-transfer events. Fully nanocrystalline films can be deposited on glass substrates using large fluxes of fast H or D atoms. (iii) 25 eV Ar+ ions modify the competitive growth of polycrystalline grains at the film surface, which leads to a coarsening of the grain structure at modest substrate temperatures.

3:20pm **TF-TuA5 Deposition Behavior and Film Characteristics of Aluminum Oxide Deposited using High Frequency Pulsed-DC Magnetron Reactive Sputtering**, ***D.C. Carter,*** *G.W. McDonough, L.J. Mahoney, G.A. Roche, H.V. Walde,* Advanced Energy Industries

The affects of pulsed-DC power application in reactive magnetron sputtering of insulating films has been the subject of much study in recent years. Improved process stability with decreased arcing incidence and cleaner films have resulted by applying bi-polar pulsed power at frequencies from 10 to 200 kHz to otherwise traditional DC magnetron reactive sputtering processes. Recent advances in power supply design, however have extended the usable range of DC pulsing to 300 kHz and above. At these extended frequencies it is observed that transient behavior in the magnetron discharge becomes increasingly dominant on the measured waveforms of the applied power. Little is known of how this behavior affects the dynamics in a reactive sputtering environment or how these high pulsing frequencies can act to influence the character of films reactively deposited. This study looks specifically at the affect high frequency DC pulsing has on reactively sputtered aluminum oxide. Target voltage and partial pressure hysteresis behavior are reviewed from 0 to 350 kHz to ascertain the affect pulsing frequency has on sputter target condition. Deposition rate and film properties of hardness and optical transmission are reviewed to better understand the impact high frequency pulsing has on the deposited material itself.

3:40pm **TF-TuA6 AC Reactive Sputtering of Dielectric Films using a Dual Magnetron**, ***A. Belkind,*** *J. Cai,* Stevens Institute of Technology; *R. Scholl,* Advanced Energy Industries, Inc.

DC reactive sputtering to produce dielectric films suffers from two problems: Arcing on the target surface and covering the anode (the 'disappearing anode problem'). Both problems have received serious attention in recent times. One way to solve both simultaneously is to apply ac power between two magnetrons. Although this approach was first suggested more than ten years ago, and has been widely implemented, a detail investigation of it is remains lacking. In this work, ac reactive sputtering from a dual magnetron system is studied. The effects of ac frequency and discharge current on reactive sputtering of aluminum oxide using both balanced and unbalanced magnetrons are investigated. Special attention is given to ion bombardment of a substrate, both electrically floating and connected to the power supply system.

4:00pm **TF-TuA7 Characterization Studies of Reactively Pulsed Magnetron Sputtered Alumina Films**, ***P.J. Kelly,*** *P.S. Henderson, R.D. Arnell,* University of Salford, UK

It is well-established that pulsing the magnetron discharge during the reactive sputtering of insulating films, particularly alumina, can significantly reduce arc events at the target. The suppresion of arc events stabilises the reactive depositon process and, thus allows control over the coating composition, structure and properties. Fully dense, defect-free ceramic films can now be routinely produced at high depositon rates using the pulsed magnetron sputtering process. However, despite the success of this process, optimum deposition conditions and the relationships between deposition conditions and film properties are not well reported. In this investigation, alumina films have, therefore, been deposited by reactive magnetron sputtering using various combinations of DC and pulsed DC power. The deposition conditions, including pulse frequency, reverse voltage and reverse time, were systematically varied, and the coatings were characterised in terms of their structures and properties. Properties measured include nanohardness, resistivity and scratch adhesion. The optical properties of the coatings have also been investigated. In addition, the power supplies and pulse units were characterised in terms of their effectiveness at arc suppression and their suitability for particular deposition processes. A range of operating conditions have been identified over which hard arcs are fully suppressed and coatings with consistent properties are produced.

4:20pm **TF-TuA8 Change in Surface Roughness with the Thickness of TiO@sub2@ Film Grown on MgO(001) by Ar-ion Beam Sputtering**, *T. Uchitani, **K. Maki**,* Yokohama City University, Japan

Thin film growth mode is closely correlated with the surface roughness as predicted from some simulation by Kim and Kosterlitz (Phys. Rev.Lett., vol. 62, 2289(1989)). According to their study, the surface roughness, R@sub a@, is proportional to d@super L@ with L = 1/(D+1), where d and L represent the film thickness and the dimension, respectively. The rutile-type TiO@sub 2@ film was deposited on air-cleaved MgO(001) held at 630 °C at 3.1 x 10@super -3@ Pa in the partial pressure of O@sub 2@ and at 7.9 x 10@super -3@ Pa in the pressure of Ar by sputtering the Ti target by Ar-ion beams accelerated at 1.2 kV. The R@sub a@ versus d relationship at d > 10 nm was determined with an AFM observation, and the film crystallinity was evaluated by determining the relationship between the intensity ratio of (110) peak of TiO@sub 2@ to (004) peak of MgO in X-rays diffraction pattern and d@super 2@. By determining the former relationship, the amount of L is estimated to be 1/2 and so D is one. In other words, the growth of TiO@sub 2@ film at d > 10 nm in the present study progresses by atom by atom process which is not accompanied with the surface diffusion for the adatoms and some atomic rearrangement in the condensed phase during the film deposition. This means that the film crystallinity is independent of d which is supported from the linear relationship between X-rays diffraction intensity peak ratio and d@super 2@.

4:40pm **TF-TuA9 Chemical Vapor Deposition of Alpha Aluminum Oxide for High Temperature Aerospace Sensors**, ***R.H. Niska,*** AlliedSignal Aerospace Co.*; A.P. Constant, T. Witt,* Iowa State University*; O.J. Gregory,* University of Rhode Island

Thin film thermocouples and strain gages are being developed for high temperature application on aerospace propulsion hardware for both development test purposes and as active control sensors. The critical technology necessary in the fabrication of the sensor is an adherent, dense, and homogeneous dielectric to provide electrical isolation at engine operating temperatures. Techniques are being developed to create a crystalline aluminum oxide dielectric formed by a combination of a thermally grown oxide [TGO] from a NiCoCrAlY hardcoating which is then enhanced with the addition of a chemical vapor deposited [CVD] crystalline aluminum oxide layer. This paper will focus on the process development used to deposit the alpha alumina layer on the TGO using CVD in a coldwall reactor at 1100C. The chemistry employed in this process is the pyrolitic decomposition of aluminum tri-isopropoxide. The hexagonal [HCP] alpha phase is achieved at deposition temperatures of 1000C-1100C, as confirmed by X-ray diffraction analysis. By eliminating gas phase and hot wall decomposition, this approach minimizes precursor depletion effects, yielding a more dense and uniform film morphology. Conformal coatings up to 10 microns thick with high resistivity and good adhesion and hardness have been observed on complex airfoil geometries. Growth rates up to 10 microns per hour are possible although low growth rates lead to more desirable film properties. The kinetics of the deposition indicate that the reaction proceeds by a mass transport limited mechanism. Uniform temperature control over highly complex geometry is desireable, but not essential for uniform film growth. Results indicate that the gas flow uniformity and the precursor transport rate are the critical variables.

5:00pm **TF-TuA10 Phase Development of Radio Frequency Magnetron Sputter Deposited Pb(Mg@sub 1/3@Nb@sub 2/3@)O@sub 3@-PbTiO@sub 3@ (90/10) Thin Films**, ***J.-K. Lee,*** Korea Institute of Science and Technology, Korea*; D.K. Park, D.-S. Cheong,* Korea Institute of Science and Technology*; J.-W. Park,* Hanyang University, Korea

The electrostrictive properties of relaxors, PMN-PT, have been the focus of intensive studies in view of their application in microactuator. This is because at around the dielectric constant maximum, relaxors exhibit large electrostrictive strain, the strain-field relationship is practically free of hysteresis, and the effective piezoelectric coefficient can be tuned by changing the magnitude of the dc bias field. PMN-PT films were deposited by r.f. magnetron sputter deposition from Pb, Mg enriched ceramic targets. The Perovskite structural analysis was confirmed by X-ray diffraction. Film growth was carried out over a wide range of processing parameters such as substrate temperature, sputtering pressures, and post annealing conditions. We focus on the formation of 100% Perovskite structured PMN-PT film with good electrostrictive properties. Composition and phase development were controlled by observing the sputter physics and the depositon mechanism. In case of the film containing the volatile species such as Pb and Mg, the sputtering pressure must be controlled. We also discuss the role of excessive MgO phase on the nanocomposite characteristics in PMN-PT films.

Vacuum Metallurgy Division
Room 620 - Session VM+MI+AS-TuA

Magnetic Recording: Head/Disk Interface and Overcoats

Moderator: Y.W. Chung, Northwestern University

2:00pm **VM+MI+AS-TuA1 Ultra Thin DLC Film as Magnetic Disks Overcoat**, ***X. Chu**, B. Zhang, K.. Johnson,* MMC Tech.

Sputtered DLC film of 100 to 200 A has been used for protective coating on thin film magnetic recording disk for years. DLC overcoat material of choice is hydrogen and/or nitrogen doped amorphous carbon deposited by magnetron sputtering. Increasing areal density in magnetic hard drives requires thinner overcoat to reduce signal loss between magnetic film and read head. Functional overcoat with thickness of 50A will be needed for next generation recording medium. Tribological performance of sputtered carbon films suffers at values below 100 A because of a degradation in physical properties. Alternative deposition techniques, such as ion-beam deposition process, create denser and harder films with the improved physical and tribological properties. In this paper we will present data on the deposition and characterization of 50 A to 30 A DLC films deposited both by sputter and IBD process. Process parameter effect on structure and mechanical properties of sputtered CNx, CHx film, and ion beam deposited CHx was studied. XPS and Raman were used to characterize film microstructure and showed the sputtered CNx film was mostly sp2 bonded. Tribology of the films were tested by Contact Start Stop (CSS) testers and the result of carbon wear can be correlated to AFM nano-wear test. 30A ion-beam deposited CHx film showed good CSS tribological performance comparable to 100 A sputtered films.

2:20pm **VM+MI+AS-TuA2 Tribological Properties of Protective Carbon Coatings Used in Magnetic Storage Devices Investigated on a Sub-Nanometer Scale**, ***A. Wienss,*** University of Saarbrücken, Germany*; G. Persch-Schuy,* IBM Germany Storage Systems Division, Germany*; U. Hartmann,* University of Saarbrücken, Germany

Ultrathin carbon coatings are used in the magnetic storage industry to protect sensitive sensor heads and magnetic media against mechanical damage. Such a damage can be modelled by artificially generated scratches using Scanning Force Microscope (SFM) techniques. Loading forces in the µN range are applied, resulting in scratches with residual depths of only a few Å. A special image subtraction technique is presented which allows careful analysis of tiny grooves even on rough surfaces. This technique compensates for drift effects during scanning. The scratching resistance of various a-C:H and CN@sub x@ films is determined. For a-C:H, an increasing amount of hydrogen results in a decreasing scratching resistance, which is a well-known behavior. Beyond a certain hydrogen content, a further increased hydrogenation causes a reproducible, slight increase of the scratching resistance. In order to explain this, the role of the friction coefficient will be discussed.

2:40pm **VM+MI+AS-TuA3 Ultrathin Overcoats For Magnetic Media: Is Hardness What We Are Looking For ?**, ***B. Marchon,*** IBM Almaden Research Center **INVITED**

As areal recording densities approach 20 Gigabit per square inch, the demand for ultrathin media overcoat (<5 nm) becomes more pressing. This talk will attempt to identify the various properties that are required to achieve good performance under increasingly severe mechanical and environmental conditions. In an attempt to bridge the process-performance gap, we will review the details of the head/disk interface system, and how the mechanical and chemical structure/properties can be optimized to achieve the required reliability. In particular, issues related to tribochemistry and interactions with the lubricant will be addressed, as well as a general discussion on what specific mechanical properties are important.

3:20pm **VM+MI+AS-TuA5 Air Bearing Collision Dynamics***, **S.E. Stupp**, R.J. Blanco, T. Riener, B.D. Strom,* Quantum Corporation **INVITED**

A few years ago, a disk drive program encountered an unusual problem: drives built with one vendor's heads (vendor A) suffered from an excessive number of thermal asperity events (TAs); drives built with head's from another vendor (vendor B) did not have as many TAs, but they did have a number of crashes. Spinstand experiments confirmed that there was a significant difference in the response of the two vendor's air bearings to collision with the 100 nm high asperities found in these drives. For example, the fly height of vendor A's heads was essentially unchanged on contact with an asperity, while vendor B's heads exhibited a fly height change (these differences may explain the drive results). The underlying problem in the drive program was ultimately traced to particulate contamination and was corrected. However, the experiments raise an interesting question: Why is there a difference in the dynamic response of the two vendor's heads? In this work we present a systematic study of this problem, which we christen Air Bearing Collision Dynamics (ABCD). The asperity collision responses of several different air bearing designs (including full rail and island type) were studied by measuring the TA signal, the change in flying height, acoustic emission (AE), and laser Doppler vibrometry, in controlled experiments on a spinstand. Since a large enough asperity can cause any head to crash, the asperity size was modest (approximately equal to the fly height). In agreement with our earlier experiments, differences in the response of the different air bearings were found. In addition, the AE signals indicate that certain island type air bearing designs can undergo multiple head-disk contacts after the asperity has passed. These results are potentially concerning, because many head vendors are moving towards this type of air bearing design. Finally, in an attempt to understand the origin of the differences in the dynamic response of different air bearing designs, we report the results of numerical modeling of the asperity and air bearing designs.

4:00pm **VM+MI+AS-TuA7 Interaction of Fluoroalcohols and Fluoroethers with Various Types of Carbon Overcoats***, **N. Shukla**, A.J. Gellman,* Carnegie Mellon University

This work is focussed on understanding the fundamentals of head-disk interface tribology at very low flying heights and higher spin rates. Since there will be room for only a single molecular monolayer of the lubricant on the disk surface at low flying heights we have studied the molecular level interaction of lubricants with carbon overcoats that protect the disk surface. We have modeled a most commonly used PFPE lubricant (Fomblin Zdol) using short chain model compounds and measured the desorption energy of these compounds on carbon films. The short chain model compounds used are 2,2,2 trifluoroethanol (CF@sub3@CH@sub2@OH) and perfluorodiethyl ether (CF@sub3@CF@sub2@OCF@sub2@CF@sub3@) which are representative of both the end group and the main chain of Fomblin Zdol. Temperature programmed desorption spectroscopy is used to measure the desorption energy of model compounds and also to understand the nature of the interaction of these short chain compounds with carbon overcoats. Initial results show that ethers interact with carbon overcoats through electron donation from the oxygen lone pair electron and the alcohols interact with carbon overcoats through hydrogen bonding. In addition we have studied the effect of various film compositions on the interaction of the lubricants in order to understand if the film composition has any effect on the nature of the bonding of the lubricant. The different types of overcoats used are hydrogenated, nitrogenated, diamond-like carbon and Ion beam sputtered overcoats. We have observed that by varying the percentage of hydrogen or nitrogen content in the film composition or by changing the carbon overcoat deposition conditions as in diamond like carbon overcoats or in an ion beam sputtered overcoat there is no significant change in the interaction of the lubricant with carbon overcoat. The alcohols however bond stronger than ethers on all overcoats, which is consistent with the structures, proposed by diffusion measurements.

4:20pm **VM+MI+AS-TuA8 Angle Resolved ESCA Methods: Molecular Conformation of Fluorocarbon Lubricant***, **M.A. Karplus**, D.J. Pocker,* IBM-SSD

Simple but useful methods for interpreting angle-resolved ESCA data from real-world samples are presented. First is a model allowing thinly-covered and thickly-covered substrate. It can be usefully applied, even in a manual fashion, with common office spreadsheets. Next, a simple slab model, with the help of canned minimization routines, can bring out subtleties in overlayer structures. Even a deeply buried monatomic layer can be isolated. The following are presented as examples. Perfluoropolyether (Zdol) lubricant on hard disk carbon overcoat shows coexisting monolayer and multilayer regions, consistent with structures identified by surface energy@footnote 1@ and ellipsometric surface diffusion@footnote 2@ measurements. Next, layering within the lubricant shows significant perfluoropolyether backbone adjacent to the overcoat surface accompanied by a discernible excess of ether oxygen. The latter facts indicate that the inverted-U conformation sometimes sketched for bonded lubricants is an exaggeration, certainly for the system studied. @FootnoteText@ @footnote 1@ G. W. Tyndall, R. J. Waltman, and D. J. Pocker, Langmuir 14, 7527 (1998). @footnote 2@ X. Ma, J. Gui, L. Smoliar, K. Grannen, B. Marchon, M. S. Jhon, C. L. Bauer, J. Chem. Phys. 110, 3129 (1999).

4:40pm **VM+MI+AS-TuA9 Airbearing Designs for High Density Recording***,* **INVITED**

Vacuum Technology Division
Room 610 - Session VT-TuA
Vacuum Contributions to the Semiconductor Industry (1950-1975)

Moderator: R.E. Ellefson, Leybold Inficon, Inc.

2:00pm **VT-TuA1 Vacuum Systems, Deposition Sources, Measurement and Control Tools for the Semiconductor Industry (1950-1975)***, **D.E. Meyer**,* Consultant **INVITED**

The purpose of this presentation is to relate and discuss how VS&T (vacuum science and technology) impacted the semiconductor industry prior to 1976. The major portion of the talk will feature research, development, production, and quality and reliability experience at Texas Instruments. But company interactions with the rest of the SC industry and the military and space agencies also provide noteworthy examples of VS&T's contributions. Initially, military requirements for performance and reliability were the driving force. Device stability and manufacturability (read yield) were key to industry growth as well. All of these it turns out were highly dependent upon equipment, processes, and control of various thin film depositions in device manufacture and vacuum techniques in package assembly. A progression of improved technology and equipment will be described including the change from filament to eb-gun deposition, from oil pumped to high vacuum dry pumped systems, process control and reliability assurance using RGA, scanning electron microscopy, and current-temperature stressing. Both early bipolar and MOS processing will be addressed. The data presented and discussed will show how significant VS&T was to the growth of the SC industry and will consist of both a review of published and unpublished information.

2:40pm **VT-TuA3 Evolution of Integrated Circuit Vacuum Processes: 1962-1975***, **R.K. Waits**,* Technical Marketing Programs **INVITED**

The quarter-century from 1950 to 1975 witnessed the introduction of an extraordinary sequence of revolutionary semiconductor products: the silicon transistor, the integrated circuit (IC), the semiconductor memory, and the microprocessor. This ever-increasing complexity was made possible by many small breakthroughs in manufacturing technology involving new fabrication processes and measurement methods. Often an innovation involving vacuum technology appeared at just the right time to make possible the next technological leap. The metallization process is a good example. The components in the first practical IC were interconnected with a patterned layer of vacuum-evaporated aluminum. When the MOS field-effect transistor was perfected, it required a sodium-free evaporation process and the magnetically-focused electron-beam evaporation source propitiously arrived to save the day. As metal connections got narrower, strange failures began to occur. The scanning electron microscope (operating under vacuum, of course) was a new tool that let us examine the surface of an IC as if we were standing on its surface and gazing around. The failures were seen to be caused by microcracks in the metal lines as they crossed over steps in the circuit topography. Geometrical analysis showed that gaps were caused by shadowing during vacuum deposition. Methods were devised increase the mobility of the depositing aluminum atoms so that they would fill in the gaps during film growth. Metallization failures due to electromigration, and the shorting of shallow junctions by silicon diffusion into the aluminum, had to be cured by adding small amounts of copper and silicon to the aluminum. New magnetron sputter sources came to the rescue. During these years, ion implantation, plasma etching, and low-pressure and plasma-enhanced chemical vapor deposition, all became manufacturing processes, and, without which, today's (and tomorrow's) ICs would not be possible

3:20pm **VT-TuA5 History of Plasma Ashing and Plasma Etching in the Semiconductor Industry from 1950 to 1975*, R.L. Bersin,*** Ulvac Technologies, Inc.

This paper will focus on the introduction of plasma etching and photoresist ashing from the late 1960's to 1975 as seen by International Plasma Corporation (IPC), the first company dedicated exclusively to the manufacture of "barrel" plasma ashers for the semiconductor industry [subsequently to be named Dionex Gas Plasma Systems, Branson IPC, and finally to disappear into Gasonics International]. The history from 1-inch wafers through 6-inch wafer development will be discussed in terms of equipment design features and process technology for both resist stripping and plasma etching. Limitations of isotropic etching and uniformity problems with barrel chambers are discussed; the introduction of the first multi-step automatic plasma ashing equipment is described. Early etching of oxide, nitride, and metals as well as stripping will be illustrated with SEM examples of the then current process technology and photographs of the equipment at that time.

3:40pm **VT-TuA6 History of Commercial Ion Implantation*, C.B. Yarling,*** EEESPEC/Ion Beam Press

In today's semiconductor manufacturing industry, doping of sub-micron junctions is impossible without the use of an ion implanter. Indeed, most process flows of advanced microprocessors and 256kb DRAMS being manufactured in modern class-10 wafer fabs contain more than 15 separate implant steps. And if one examines the National Technology Roadmap for Semiconductors (NTRS), it is clearly seen that the implanter continues to play a key role in an industry that has been richly filled with people and equipment. A historical perspective of ion implantation begins with its development in 1906, when Rutherford bombarded aluminum foil with an alpha particle, and ends in 1978, when it is generally considered that ion implanters came of age! Sandwiched between these two events are several key process and equipment developments: Schockley's patent on ion implantation (1954); delivery of the first industrial implanter (1960); the first doping implant in semiconductor manufacturing (1962); shipment of the first US commercial implanter (1967); and the first semiconductor wafer fab to use implantation on all devices (1970). This paper reviews the history of ion implantation, the genealogy of commercial implanter manufacturing companies, and visits some of the colorful people who have helped to make the industry what it is today. We see that a certain amount of incestuousness has enabled this industry to grow since its inception. Yet in today's business climate where acquisitions and mergers are the norm rather than the exception, we find only three remaining major US suppliers of ion implanters. Although new shallow doping technologies which may eventually replace some implant steps are being developed, it is clear that the ion implanter has enabled semiconductor technology to travel the NTRS roadmap, where microns of junction depths in the mid-1960's are now in the sub-micron regime at the start of the new millennium.

4:00pm **VT-TuA7 Application of Sub-atmospheric Plasmas to Semiconductor Device Processing*, D.M. Mattox,*** Management Plus Inc.

Sub-atmospheric pressure plasmas play a critical role in semiconductor device processing. Plasmas provide the ions used to sputter surfaces, modify film properties and affect the surface coverage by deposited films. Plasmas also 3activate2 reactive species to enhance chemical reactivity for reactive cleaning, deposition and etching processes. This paper reviews the history of using plasmas for surface preparation, PVD and PECVD film deposition, modification of film properties, reactive deposition and plasma etching to create film structures.

4:20pm **VT-TuA8 Refining Old Vacuum Knowledge for Today's Semiconductor Manufacturing Processes*, J.F. O'Hanlon,*** University of Arizona **INVITED**

In today's competitive manufacturing environment, it is necessary to use vacuum system processes which are reliable, repeatable and cost efficient. This knowledge which constitutes our understanding of vacuum science is vast, and has on occasion been forgotten or misused. This talk will review some important concepts which have been re-invented, or re-applied or misunderstood in the course of designing modern vacuum-based processing systems.

Applied Surface Science Division
Room 4C - Session AS-TuP
Poster Session

AS-TuP1 Pattern Measurements of Reticles with Optical Proximity Correction Assist Features Using the Atomic Force Microscope*, K.-J. Chao,* ***R.J. Plano****, J.R. Kingsley,* Charles Evans & Associates*; F. Chen, R. Caldwell,* MicroUnity Systems Engineering, Inc.

A 4X, 6-inch reticle with optical proximity correction (OPC) assist features intended for deep ultraviolet (DUV) exposure was investigated. A set of chrome lines with designed CD (linewidths in this case) from 0.24 to 2.00 microns was profiled by AFM. The goal of this work is to present a method to ensure consistent measurement of chrome lines widths on the reticle. This is done by consistently measuring the line width at the half-height position on the line cross-section, i.e., full width at half maximum (FWHM). defining the boundaries of the line width at the half height locations of the edge steps. Using this method, the CD linearity is found to be within ±20nm over a range of line widths from 2.00 um to 0.4 um. Additionally, the CD uniformity is found to be worse when the widths of the lines are nominally less than 0.4 um.

AS-TuP2 Changes in the Performance of a Cylindrical Mirror Analyzer Induced by Sputter Depth Profiling*,* ***M. Kottke****,* Motorola, Inc

Optimum performance of a cylindrical mirror analyzer (CMA) is dependent upon proper fringe field correction at both ends of the concentric cylinders. In many CMAs this fringe field correction is accomplished with concentric metal rings deposited on the surfaces of solid ceramics which completely seal off the ends of the analyzer. This paper describes the degradation in performance of the analyzer caused by the redeposition of sputtered secondary ions onto the surface of the conical ceramic at the input of the CMA. It will be shown that the time frame of this degradation varies widely from days to months (or even years) depending on the materials being analyzed and the mode of operation of the CMA. It will also be shown that the loss in integrity of the fringe field correction causes large changes in the energy transmission function of the analyzer. Errors in quantitative calculations based on the use of elemental sensitivity factors determined from standards run on a specific instrument at a fixed point in time can therefore be proportionately large. Alternate modes of operation which minimize degradation are presented along with a discussion of alternate fringe field correction schemes.

AS-TuP3 Formation of Dioptase-like Structures in Silica Xerogeles Doped with Copper*,* ***F. Ruiz****, J.R. Martinez-Mendoza,* Universidad Autonoma de San Luis Potosi, Mexico*; J. Gonzalez-Hernandez,* CINVESTAV-IPN, Mexico

Using IR absorption and Raman spectroscopy we have analyzed the incorporation of Cu in SiO@sub 2@ matrix in samples prepared by the sol-gel method. Samples contain Cu at 30 %wt and were studied as a function of annealing temperature. It is found that the heat treatments have a remarkable influence on the structure. With this analysis we inferred that the final structure of the sample contain dioptase-like structures (Cu@sub 6@[Si@sub 6@O@sub 18@]*6H@sub 2@O).

AS-TuP4 Reaction of Fluorocarbon Contaminants with Aluminum Oxides: Inadvertant Fluoride Formation during Low Temperature Plasma Cleaning of Aluminum Alloy Surfaces*,* ***C.E. Moffitt***[1]*, D.M. Wieliczka,* University of Missouri, Kansas City*; C.M. Reddy, Q. Yu, H.K. Yasuda,* University of Missouri, Columbia

Plasma deposited films have shown promise as intermediate adhesion and barrier layers for use in the interface engineering of corrosion protection systems on various materials. The surface treatment of plasma deposited trimethylsilane (TMS) films with fluorocarbon plasmas has been seen to significantly improve the adhesion of certain paints to these films, which are strongly adhered to underlying aluminum alloy substrates. Oxygen plasma cleaning of the alloy surfaces, prior to deposition of the TMS film, is normally employed to remove organic contaminants. During testing, one batch of aluminum panels was processed without the oxygen plasma treatment and exhibited extensive adhesion failures. An investigation of these results shows that low levels of fluorocarbon contaminants readily react with the alloy surface and deposit a carbonaceous layer, which dramatically interferes with the adhesion of the plasma polymer to the alloys. XPS studies show that the presence of even low levels of these contaminants in the chamber, during the oxygen cleaning process, is sufficient to induce the conversion of the surface from oxide to a mixture of oxide and fluoride. When present, this fluoride layer is found to reduce the corrosion resistance of test panels. Support for this work was provided by DARPA under U.S. Air Force contract F33615-96-C-5055.

AS-TuP5 Photodegradation and Direct Patterning of PVDF and P(VDF-TrFE) using Sychrotron-based X-rays*,* ***P.T. Sprunger****, J. Choi, E. Morikawa, H. Manohara,* Louisiana State University

Upon hard and soft X-ray exposure from a synchrotron storage ring, the photodegradation and direct patterning of PVDF and copolymer P(VDF-TrFE) thick and thin films have been studied with ultraviolet photoemission and mass spectroscopy. After exposure of soft white light X-rays (<1 keV) on crystalline, 5 ML P(VDF-TrFE) films, ultraviolet photoelectron spectroscopy reveals that the photodegradation mechanism involves both an increase in the carbon conjugation (single to double bond formation). With increasing illumination amount of white light, new valence band features emerge near and cross the Fermi level. Furthermore, there is an attenuation of the fluorine 2s core-level intensity due to photodetachment. The photodetached components of the copolymer, as detected with mass spectroscopy, are hydrogen, fluorine, and HF. This photodegradation mechanism affords the ability to direct patterning of PVDF and P(VDF-TrFE) using X-rays. Without the use of any reactive chemical gas, a maximum etched depth in excess of 9 mm is achieved using hard X-rays (2 keV to 16 keV) in thick, amorphous films of PVDF. The ability to pattern PVDF, a piezoelectric, pyroelectric and ferroelectric polymer, has potential applications in the areas of micro-sensors, actuators and non-volatile ferroelectric random access memory (NVFRAMS) technology.

AS-TuP6 An Ellipsometric Study of Plasma Deposited Thin Films*,* ***T. El-Agez****, C.E. Moffitt,* University of Missouri, Kansas City*; H.K. Yasuda,* University of Missouri, Columbia*; D.M. Wieliczka,* University of Missouri, Kansas City

Spectroscopic ellipsometry was used to study films produced from a plasma of trimethyl silane gas deposited on silicon substrates. In addition to the as formed plasma film, the film surfaces were treated with either an oxygen or nitrogen plasma. Ellipsometric measurements were made on the films within 1 day after deposition and as a function of time, to determine the influence of atmospheric conditions. Additionally, the films were exposed to ultra-violet light and the changes were again tracked as a function of time. Several models were used to analyze the ellipsometry results with all of them taking into account the silicon substrate and oxide layer. One kept the overall film thickness constant, i.e. the oxide grew into the deposited film. Another assumed the plasma deposited film was stable but with additional film growth due to the oxidation. And the last allowing for both film growth and modification of the plasma film. The results obtained from these models were correlated to x-ray photoelectron spectroscopy results.

AS-TuP7 Surface-attached Polymer Brushes via Physisorbed Monolayers of Macroinitiators*,* ***T. Stöhr***[2]*, J. Rühe,* Max-Planck-Institute for Polymer Research, Germany

Block copolymer adsorption is a frequently used procedure to modify the surface of solid substrates.@footnote 1@ Such systems, usually A-B block copolymers, consist of an anchor block which allows attachment to the substrate surface and a buoy block which carries the desired surface properties. Since one part of the molecule has to have only a weak interaction with the surface and the other a strong one, the two blocks should be rather different from a chemical point of view. This renders the task of finding a suitable solvent process non-trivial. Monolayers prepared by this technique are inherently very thin with thicknesses typically between 3 and 5 nm. The reason for this is a kinetic hindrance for the attachment of polymer chains due to a diffusion barrier created by the already attached molecules. Recently radical polymerization using chemisorbed azo-type initiators has been established.@footnote 2@ In this case the polymer is grown directly at the surface of the substrate. We present a macroinitiator system that allows to create hydrophobic layers on hydrophilic substrate surfaces. Here a hydrophilic anchor block bearing initiator groups is physisorbed to a hydrophilic surface. The hydrophobic buoy block is polymerized in situ resulting in a block copolymer monolayer. A poly(epsilon-caprolactone) macroinitiator containing azo moieties was synthesized and adsorbed to silicon oxide surfaces. The surface-attached monolayer was subsequently used for the polymerization of n-alkyl methacrylates resulting in thicknesses up to 100 nm. By this route the limitations of the block copolymer physisorption process, such as solubility problems of the block copolymer and intrinsic limitations of the layer

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

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

thickness, can be overcome. @FootnoteText@ @footnote 1@ Fleer, G. J.; Cohen Stuart, M. A.; Scheutjens, J. M. H. M.; Cosgrove, T.; Vincent, B. Polymers at Interfaces; Chapman & Hall: London, 1993; Chapter 6. @footnote 2@ Prucker, O.; Rühe, J. Macromolecules 1998, 31, 592.

AS-TuP8 Observing Damage Produced during XPS Measurements*, **M.H. Engelhard**, D.R. Baer, G.C. Dunham,* Pacific Northwest National Laboratory

An increasing amount of studies in our laboratory involve analysis of polymers, self assembled monolayers (SAMS) with different terminations, insulators and other materials for which some properties of the specimens degrade with time during x-ray exposure. When damage is observed, a series of parameter tests are conducted to determine the conditions and time for which reliable data can be collected. In this paper we will report measurements made on SAMS with CH@sub 3@, OH and COOH, as well as some test coupons of PCEMA, PTFE and PVC. Most of these measurements were made on a Physical Electronics Quantum 2000 for which a variety of different x-ray flux densities can be arranged. In addition, the beam can be moved around to examine the regions over which damage occurs. Measurements for COOH terminated SAM show a damage production directly related to the flux per unit area. These, and other results, suggest that damage on many materials is not simply due to specimen heating. However, tests on PCEMA show damage to occur outside the region that was exposed to the x-ray beam. These tests will be described along with a new series of experiments being undertaken to determine if specimen cooling provides a way to decrease specimen damage. This work was conducted in the W. R. Wiley Environmental Molecular Sciences Laboratory, a national scientific user facilty sponsored by the U. S. Department of Energy's Office of Biological and Environmental Research.

AS-TuP9 Role of Temperature in the Surface Oxidation Chemistry of IN-738 Superalloy*, **L. Bracho**[1], S. Seal, V. Desai,* University of Central Florida

Super-alloys are used in high temperature industrial applications because of their strength, high resistance to high-temperature oxidation and hot corrosion, and longer durability than other conventional alloys. Although super-alloys possess these characteristics, they are still subjected to high temperature degradation when exposed to aggressive environments. The current research includes the high temperature oxidation behavior of IN-738 at 850, 900, and 950°C in air for a period of 300 consecutive hours. The oxidation kinetics is parabolic in nature. Due to its parabolic nature, the lattice diffusion is prominent in the various oxide formations. This leads to selective oxidation of various elements present in the alloy. The decrease in oxidation rate observed at higher temperatures is due to more alumina formation. The surface oxide formation is investigated using using XPS, AES, XRD, SEM, and EDS. It is expected to find external oxides rich in chromium, aluminum, nickel, and titanium. The thickness of the oxide and the gamma' depleted layers are expected to increase with temperature.

AS-TuP10 Noncontact AFM Imaging of Al-Adsorbed Si(111) Surface*, **S. Orisaka**, T. Minobe, K. Makimoto, Y. Sugawara, S. Morita,* Osaka University, Japan

Recently, several groups including ourselves have reported true atomic resolution imaging using noncontact atomic force microscope (NC-AFM) operating in ultrahigh vacuum. In order to apply the NC-AFM as a scientific tool in variety of fields such as surface science, it is very important to understand the imaging mechanism of the NC-AFM on various sample surfaces. On the Si(111)7x7 reconstructed surface, we clarified that the tip-sample interaction force is dominated by the chemical bonding interaction between the dangling bond out of the Si tip apex and the dangling bond on Si adatom on the surface. In the present experiments, we investigated force interaction between an orbital of a dangling bond out of a Si tip apex and an empty orbital on a sample surface. As a sample surface with empty orbitals, Al-adsorbed Si(111) surface was used. We obtained strong contrast of NC-AFM images on Al-adsorbed Si(111) surface. Furthermore, we observed the characteristic discontinuity in the distance dependence of the frequency shift. So far, similar discontinuity has been observed on Si(111)7x7 surface, and it can be explained by the chemical bonding interaction between the dangling bond out of the Si tip apex and the dangling bond on Si adatom. So, the discontinuity in the distance dependence of the frequency shift on Al-adsorbed Si(111) surface seems to be originated from the chemical bonding interaction between an orbital of a dangling bond out of a Si tip apex and an empty orbital on a sample surface.

AS-TuP11 Characterization of Chemically Heterogeneous Samples Using XPS Imaging and Small Area Analysis*, **A.C. Ferryman**[2], J.E. Fulghum,* Kent State University

Recent advances in XPS instrumentation allow for the rapid acquisition of photoelectron images with a spatial resolution of a few microns. This capability both expands the range of samples which can be characterized using XPS, and provides additional complications in data interpretation and analysis. For samples which have a surface roughness comparable to the depth- of-focus within the image, care must be taken to distinguish between surface roughness effects and changes in chemical state or elemental distribution. Sandstones coated with a commercial perfluoropolyether for protection from weathering were characterized using imaging and small area XPS. Polymer impregnation into the stone, and uniformity of the polymer coating were characterized through analysis of both cross-sections and the surface of the sandstone. Variations in polymer distribution on both macro- and micro-scales will be discussed and evidence for polymer segregation between components of the sandstone evaluated. This system provides an example of the information which can be obtained, and artifacts which must be considered, in the analysis of a chemically heterogeneous sample which also contains significant surface roughness.

AS-TuP12 Characterisation of Oxide on GaAs Wafer Surfaces with TOF-SIMS and ARXPS*, **B. Burkhardt**, O. Brox,* Universität Münster, Germany*; W. Fliegel,* Freiberger Compound Materials GmbH, Germany*; L. Wiedmann,* Universität Münster, Germany*; A. Kleinwechter,* Freiberger Compound Materials GmbH, Germany*; A. Benninghoven,* Universität Münster, Germany

Molecular-beam epitaxy (MBE) on GaAs requires a thermally removable oxide. Therefore reliable techniques are needed to control oxides on the GaAs wafer surface in the production process. The quantitative oxide characterization (thickness and stoichiometry) can presently only be achieved by ARXPS. In this paper we compare results achieved with TOF-SIMS and ARXPS. The experiments were performed in a reflectron based TOF instrument equipped with an 8'' manipulator for macroscanning and a dual beam source for depth profiling (sputter beam: 500eV Cs@super +@, analysis beam: 10kV Ar@super +@). For ARXPS we used a spherical electron analyzer with multichannel detector and monochromator X-ray source (Al K@alpha@: 1486,6 eV). For ARXPS data interpretation we assumed a 4-layer-system for the GaAs oxide. Separating the XPS signal into different oxide states we determined thickness and stoichiometry of each layer. Dual beam depth profiling was used to characterize the oxide layer by means of SIMS. The integrals of the secondary ions AsO@sub n@@super -@ and GaO@sub n@@super -@ over the sputter depth can be correlated to the oxide thickness and the various oxide phases as identified by ARXPS. The use of SF@sub 5@@super +@ primary ions allowed the detection of Ga@sub m@As@sub n@@super ±@ cluster ions with more than 40 atoms. The Ga/As ratio of these clusters changes with storage time and can be taken as a measure of stoichiometry changes in the uppermost atomic layer. Using ARXPS for calibration TOF-SIMS has shown to be a suitable technique to control the oxide layer on GaAs wafer.

AS-TuP13 Surface Energy Change and Hydrophilic Formation of PE, PS and PTFE Films Modification by Hydrogen Ion Assisted Reaction*, **J. Cho**, K.H. Yoon,* Yonsei University, Korea*; S.K. Koh,* KIST, Korea

The Polyethylene (PE), Polystyrene (PS) and Polytetrafluoroetyhylene (PTFE) surface modification has been investigated by hydrogen ion assisted reaction with oxygen environment. The IAR is a kind of surface modification technique using ion beam irradiation with reactive gas environment. The hydrogen ion beam energy was 1 keV, ion dose were varied from 5ï,´1014 to 1ï,´1017 ions/cm2, and amount of oxygen blowing gas fixed 4 sccm (ml/min). Wettability was measured by water contact angles of water contact angle measurement, and the surface functionality was analyzed by x-ray photoelectron spectroscopy. The contact angle of water to PE modified by argon ion beam only decrease from 95 to 52 degrees, and surface energy was not changed significantly. But, the contact angle using hydrogen ion beam with 4 sccm oxygen environment was stiffly decreased to 8 degree and surface energy 65 ergs/cm. In case of PS, the contact angle and surface energy changes were similar results of PE, but the contact angle of PTFE samples decreased with ion dose up to 1ï,´1015 ions/cm2, increased at higher dose, and finally increased to the extent that no wetting was possible at 1ï,´1017 ions/cm2. The PTFE samples irradiated with argon with oxygen environment had lower contact angle than hydrogen with oxygen, even though the samples with oxygen environment

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

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

developed hydrophilic groups on the irradiated surfaces. This results was due to the hydrogen ion beam that affect the surface cleaning for removing the impurities on PE surface and, then hydrogen ion beam was activated with C-H bonding to make some functional groups in order to react with the oxygen gases, finally, unstable PE surface can be changed from hydrophobic to hydrophilic formation such as C-O and C=O from the XPS analysis, and the ion assisted reaction is very effective tools to attach reactive ion species to form functional groups on C-C bond chains of PE.

AS-TuP14 Control of Intracellular Signal Transduction Using Self-Assembled Monolayers of Alkylthiolates on Gold*, K.B. McClary*[1], *D.G. Grainger,* Colorado State University

Self-assembled monolayers of terminally-functionalized alkylthiolates on gold have been used to interrogate cell-biomaterial surface interactions at the extracellular and intracellular level. The goal of this research is to provide molecular level information on the surface determinants necessary to produce predictable, controllable biological responses to implanted materials. Various aspects of "outside-in" communication between cells and material surfaces have been investigated. Formation of focal contacts and stress fibers, early indicators of effective intracellular signaling, was observed to be surface-chemistry dependent, and correlated with protein behavior on different surface chemistries. The primary cellular regulators of these events were examined using well-controlled alkylthiol surface chemistries. Activation states of the GTPase RhoA were determined and shown to be surface chemistry-dependent. RhoGDI levels and intracellular localization were also shown to be surface-chemistry dependent. Cells cultured on -CH3 terminated SAMs, which normally exhibit a low growth phenotype, were transfected with a constitutively active RhoA mutant. Transfected cells exhibited significant increases in cell length. However, no focal contact formation was observed. These results show that genetic alteration of intracellular regulators is incapable of overcoming the lack of extracellular stimuli, in the form of adsorbed ECM proteins, present on -CH3 terminated SAM surfaces. In summary, extracellular and intracellular information indicates that surface chemistry is capable of modulating communication between a cell and its extracellular environment. These data provide new, valuable molecular level information necessary to develop rational cause and effect relationships between a material's surface chemistry and biological response.

AS-TuP15 Core-level Satellites and Outer Core-level Multiplet Splitting In Mn Model Compounds*, A.J. Nelson,* *J.G. Reynolds,* Lawrence Livermore National Laboratory*; J.W. Roos,* Ethyl Petroleum Additives

We report a systematic study of the 2p, 3s and 3p core-level photoemission, satellite structures and valence bands of Mn model compounds. Charge-transfer from the ligand state to the 3d metal state is observed and is distinguished by the prominent shake-up satellite about 5 eV higher than the Mn 2p@sub 3/2@ peak for of all the Mn@super +2@ species and MnPO@sub 4@. The Mn 3s final state configuration can be either 3s3d@super 5@ or 3s3d@super 6@L depending on final state screening effects due to the ligand. We observe that the Mn 3s multiplet splitting becomes smaller as the Mn oxidation state increases, except for the Mn-phosphate species. Also, the 3s final state has @super 7@S and @super 5@S symmetry. In the @super 7@S state, the remaining 3s electron is well correlated with 3d electrons of parallel spin, while in the @super 5@S state the two spins are antiparallel. This electron correlation reduces the branching ratio of the @super 7@S:@super 5@S states as experimentally observed. In addition, as the ligand electronegativity decreases, the spin state purity is lost in the 3s spectra and the spectra becomes representative of mixed unscreened (3d@super N@) and locally screened (3d@super N+1@) final states. Our results are best understood in terms of configuration-interaction (CI) calculations including intrashell electron correlation, charge-transfer and final-state screening.

AS-TuP16 Optimizing Signal Intensities in REELM and SAM Microscopies: A Comparision of Instruments Operated in Fixed-Analyzer-Transmission (FAT) and Fixed-Retard-Ratio (FRR) Modes*, E. Paparazzo,* *L. Moretto,* Consiglio Nazionale delle Ricerche, Italy*; S.A. Lea, D.R. Baer,* Pacific Northwest National Laboratory

Signal intensity is the main factor for chemical contrast in reflected electron energy loss microscopy (REELM) and scanning Auger microscopy (SAM) images of surfaces. We report here on REELM and SAM signal intensities measured as a function of the primary beam energy (Ep) for two Auger microprobes: one operated in the fixed analyzer transmission (FAT) mode (Cameca 'Nanoscan 50', Rome), the other in the fixed retard ratio (FRR) mode (PHI '680 Auger Nanoprobe', Richland). The aim of this work is to quantitatively determine the extent to which each type of microprobe affects the relative intensities of REELM and SAM signals. To accomplish this task we conducted a comparative analysis in the two laboratories using atomically-clean Al metal as a sample. We measured the intensity ratio between the first bulk plasmon signal and the Auger Al LVV signal (KE ~ 70 eV) as a function of Ep, which was chosen at several values within the range 200-2000 eV. We found that for both the FAT and FRR microprobe this ratio decreases by a factor ~ 10 upon increasing Ep from 200 to 2000 eV. These findings are discussed in light of both the energy resolution and response function associated with the FAT and FRR operation modes in the KE range considered, and they are used to account for the chemical contrast of REELM and SAM images acquired in the two microprobes at differing Ep's. We show that our work can help devise an optimal compromise between chemical contrast, surface-specificity and chemical speciation in both REELM and SAM imaging, whether the two methods are performed in FAT or FRR Auger microprobes.

AS-TuP17 The Develpment and Application of a High Speed Etching Source for Destructive Depth Profiling*, A.J. Roberts,* *C.J. Blomfield, S.C. Page, D.J. Surman,* Kratos Analytical, UK

The development and application of a low energy argon ion beam source for destructive depth profiling, combined with X-ray photoelectron spectroscopy (XPS) are presented. This compact Kaufman ion source which combines extremely high sputter rates and low ion beam acceleration potentials, reduces ion induced mixing of the surface atoms. The properties of this ion source mean that concentration depth profiling through several hundred nanometer thick layers is possible, whilst retaining good interface resolution. Rotation of samples during sputter profiling is shown to improve interface resolution. The depth profiling capabilities of this high speed etching source will be demonstrated through a number of challenging samples. Atomic concentration profiles through a three layer sample have been performed as a function of ion acceleration voltages, and the effect on interface resolution is discussed. A further example of depth profiling through an inorganic material with a thin metal underlayer on polyester is shown. Chemical state information is retained from the inorganic oxide layer, with some reduction of the oxide layer observed due to the preferential sputtering of oxygen from the surface during profiling. Data presented shows no decrease in the sputter rate due to positive charging of electrically insulating samples during the sputtering process.

AS-TuP18 A Dual Anode Monochromatic X-ray Source*, S.C. Page,* *C.J. Blomfield, B.J. Tielsch, D.J. Surman,* Kratos Analytical, UK

High energy Ag L@alpha@ X-rays have several advantages over the more commonly employed Al K@alpha@ source. A photon energy of 2984.3eV means that a Ag source can generate higher energy core levels, Auger series and has a greater excitation volume. A further advantage over other high energy sources is that the Bragg condition may be satisfied via a second order diffraction within the confines of the conventional Al K@alpha@ monochromator body with only minor modifications. We have now for the first time implemented a Ag monochromator as a modification to the standard Al monochromator on a modern magnetic lens based electron spectrometer, the Axis Ultra. The anode of the Al monochromator has been adapted to have both a conventional Al face as well as an additional Ag face, thus changes between source may be made by minor adjustment without breaking vacuum. The great improvement gained in photoelectron collection efficiency by employing magnetic lens technology improves the sensitivity and ultimate usability of the Ag source making it a viable alternative for the measurement of deep 1s core levels and Auger parameters. The results presented show the performance of the Ag source to give resolution better than 0.9 eV FWHM on Ag and a sensitivity greater than 4,300 CPS on Au at a resolution of 1.3eV. Further results highlighting the usefulness of the source on practical samples will be presented.

AS-TuP19 Scanning Tunneling Microscopy and X-ray Photolectron Spectroscopy Studies of WO3 Thin Films Submitted to Various Thermal Treatments in Air and Ultra High Vacuum*, S. Santucci,* *L. Lozzi, M. Passacantando,* University of L'Aquila and INFM, Italy*; L. Ottaviano,* INFM, Italy*; C. Cantalini, L. Odorisio,* University of L'Aquila, Italy

The gas sensitive properties of WO3 thin films seem to be due to a loss of oxygen at the surface, which determines the presence of active sites for the reaction with gases (Co,NOx,ozone). The reactivity of the WO3 films is strongly influenced by the morphology and surface properties. In this work the surface electronic and structural properties of about 150 nm thick WO3 films, deposited in high vacuum by thermal evaporation onto Si substrates, have been studied in UHV by means of XPS and Scanning Tunneling

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

Microscopy/Spectroscopy (STM/STS). After the deposition these films have been annealed in atmospheric owen for 24 h at different temperatures (300 and 500° C) to stabilise the film morphology. The XPS measurements, by using a monochromatic Al source to follow W 4f, O 1s peaks and the valence band, have been performed on these samples both as prepared and after a re-annealing in UHV at temperatures ranging from 50 to 600 ° C, . The UHV re-annealing procedure strongly modifies the W 4f peak of both the as deposited and 300 ° C samples, showing the loss of oxygen. Moreover, at the Fermi edge, before the UHV annealing there is a small signal due to the presence of metallic states. This signal after the UHV annealing strongly increases, indicating the presence of an high density of states at the Fermi edge. Instead the 500 ° C sample, after the heating in UHV has shown a substantial stability of the nearly stoichiometric WO3 phase. Using STM in UHV we have investigated the morphology of the samples at room temperature and while scanning at elevated temperatures up to 600 °C. In particular we have simoultaneously taken I-V curves at the boundaries and centers of the typical grains of the polycrystalline sample. Our findings on the electronic structure of the samples close to the Fermi level are in agreement and allow clearer understanding of the findings from a parallel XPS study.

AS-TuP20 Radiation Damage Study of n-Alkanethiols Deposited on Platinum*, N. Franco*, *T. Van Buuren, C. Bostedt, L.J. Terminello,* Lawrence Livermore National Laboratory

The potential technological applications of Self Assembled Monolayers (SAM's) has increased dramatically in the past few years. Most of these applications exploit the flexibility and simplicity of the monolayer film growth. Alkanethiols adsorbed on nobel metals are perhaps the best example of theses ordered interfaces and, in these cases, it has been shown that the stability of the adsorbed molecules is strongly related with the dimension of the carbon chain. We performed valence band and core level synchrotron radiation spectroscopy studies of different n-alkanethiols adsorbed on platinum in order to investigate the stability of these films under a Ultra Violet (UV) or soft X-ray exposure. Additionally we measured the change in the empty states by X-ray Absorption Spectroscopy (XAS) and we imaged the surface by Atomic Force Microscopy (AFM) to determine surface morphology. We will present results that suggest a change in the structure of the molecules adsorbed caused by irradiation. This change is related to the photon flux and is not energy dependent. @FootnoteText@ C. Bostedt is supported by the German Academic Exchange Service DAAD, N. Franco by the Spanish education and culture office. The work is supported by the US-DOE, OBES Material Sciences under contract W-7405-ENG-48, LLNL.

AS-TuP21 Surface-initiated Anionic Polymerization: Investigation of Functionalized Surfaces and In-situ Polymer Films*, R.C. Advincula,* University of Alabama at Birmingham, US*; Y. Nakamura, S. Inaoka, Q. Zhou,* ***J. Mays,*** University of Alabama at Birmingham

The surface initiated anionic polymerization is a "grafting from " approach to tethering polymer chains to surfaces. Although various surface-initiated polymerization schemes have appeared recently, we seek to utilize the anionic polymerization approach with its potential to forming monodispersed polymers of controlled MW through "living" polymerization. In this report, we describe the synthesis of the initiator; diphenylethylene (DPE) silane derivative, the activation towards initiation, polymerization mechanism, and characterization of the polymers bound on the substrate. An important focus is the analysis of the substrate before and after formation of the self-assembled-monolayer (SAM) of the initiator. We have utilized electrochemical methods, contact angle, quartz crystal microbalance (QCM), ellipsometry, atomic force microscopy (AFM), and surface plasmon resonance spectroscopy (SPS) to characterize the surfaces. We then correlated the initiation and the polymerization mechanism with the properties of the functionalized substrate. In particular we were interested in observing the density and distribution of the initiating species on the surface in a mixed system (alkylsilane) We have observed a dependence on the domain size and mixture composition of the initiator to the microstructure and physical properties of the resulting polymer (polystyrene and PMMA) films. Further characterization will be done on the polymer films by scale-up (using silica particles) and detachment from the surface.

AS-TuP22 Surface Limiting Factors of the Growth of Metallic Nanoparticles*, R. Tannenbaum,* Georgia Institute of Technology*; H. Rotstein, A. Novick-Cohen,* Technion-Israel Institute of Technology, Israel

Chemical synthesis of metal clusters, unlike UHV methods, offers a great deal of flexibility in manipulating cluster properties, such as the oxidation state and the reactivity of the metal clusters due to particle size variations, all within the bounds of the nanoscale regime. Stabilization and control of the size of metallic colloidal particles are achieved in polymer solutions, due to the adsorption of the polymer to the coagulating metal fragments, to form a layer which separates the particles sufficiently in order to keep van der Waals forces below thermal energy levels. Among the most promising chemical avenues, is the thermal decomposition of metal carbonyls in the presence of polymers with relatively low reactivity (e.g. polystyrene) under controlled inert atmosphere, resulting in the formation of zero-valent metallic particles. During the decomposition reaction of the metal carbonyl precursors highly reactive intermediates are formed, resulting in two major subsequent reaction pathways: (a) Aggregation to form small clusters; and (b) Interaction with the polymer. The final particle size and particle size distribution will be a direct function of the various facets of this complex mechanism. For the growth of zero-valent cobalt clusters, there is an inverse correlation between cobalt cluster particle size and the polystyrene concentration in the reaction solution. The increase in the concentration of polystyrene in solution will result in an increase of the concentration of the adsorbed polystyrene layer, and hence a decrease in the final cobalt cluster size. The thickness of the adsorbed polymer layer is calculated by using a combination of TEM and STM measurements. The difference in the particle size diameters calculated by the two methods provide an indication of the thickness of the polymer layer. We will present working models for the correlation between the final cobalt nanocluster size and the extent of metal-polymer surface interactions.

AS-TuP23 Time-Resolved Observations of Failure along Polymer-Glass Interfaces in Humid Environments@footnote 1@*, J.T. Dickinson,* *N.Z. Hertelendy, S.C. Langford,* Washington State University

Adhesive interfaces play a critical role in microelectronic packaging, as well as in aerospace, automotive, and civil structures. The accelerated failure of strained adhesive bonds due to moisture is of considerable interest. By studying very small bonded zones (area @<=@ 1 mm@super 2@) one greatly enhances the influence of environmental attack, allowing for accelerated testing. To measure failure kinetics, we compare videotaped micrographic records of failure along ethylene vinyl acetate/soda lime glass interfaces in humid atmospheres with simultaneously acquired measurements of applied force. The interface is viewed through the glass substrate with an optical microscope. With increasing applied stress and relative humidity, the time required to produce an observable defect and the total time to failure decrease in a monotonic fashion. With increasing stress, the size of the crack at the onset of unstable critical crack growth also decreases. Visible crack growth prior to unstable failure is rate limited by the diffusion of water to the crack tip. The time required to produce a visible defect can be accounted for on the basis of chemically assisted failure, where the crack velocity depends directly on the change in surface energy due to water sorption (not transport limited). A quantitative model for the dependence of failure on stress and humidity is presented. @FootnoteText@ @footnote 1@This work is supported by the NSF Surface Engineering and Tribology Program under Grant CMS-98-00230.

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Poster Session

BI-TuP1 Characterization of Adsorbed Protein Films by Static Time of Flight Secondary Ion Mass Spectroscopy (ToF-SIMS)*, M.S. Wagner,* *J.B. Lhoest, D.G. Castner,* University of Washington

The development of effective biomaterials requires knowledge about the composition and structure of the adsorbed protein film that is formed upon implantation of a biomedical device in the body. Static Time of Flight Secondary Ion Mass Spectroscopy (ToF-SIMS) is a powerful technique for probing the molecular structure and composition of the outermost layers of a surface, making it an ideal technique for characterizing adsorbed protein films. Previous static ToF-SIMS studies of adsorbed protein films have shown the data obtained are complex fragmentation patterns arising from the amino acids present in proteins. To efficiently utilize all the information in these complex spectra requires multivariate analysis methods. We have used Principle Component Analysis (PCA) and Partial Least Squares (PLS) regression of the static ToF-SIMS data to characterize the composition of adsorbed protein films on mica and Teflon surfaces. PCA was used to differentiate the pure films of various plasma proteins (albumin, fibronectin, fibrinogen, etc.). PLS regression was used to quantitate the surface composition of protein films resulting from the competitive adsorption of binary protein mixtures comprised of albumin/fibronectin and albumin/Immunoglobulin G. For the albumin/fibronectin mixtures it was found that solutions containing more than 20% fibronectin produced adsorbed protein films that appeared to be pure fibronectin. The static ToF-SIMS results could be quantified by calibrating them with radiolabeled protein adsorption results. The overall aim of this research is to generate of a ToF-SIMS spectral database that can be used to determine the composition and structure of multicomponent adsorbed protein films with static ToF-SIMS.

BI-TuP2 Immobilization of Proteins on Self-Assembled Monolayers by Electrostatic Interactions*, **Y. Du**, S.S. Saavedra,* University of Arizona

Immobilization of proteins onto solid substrates has been studied widely because of the importance of biomolecular films molecular devices. Adsorption of protein molecules onto solid surfaces by physical interactions is technically simple immobilization methods. However, in order to form highly ordered protein films, a single type of site-directed binding must be employed. In this study, sulfonated silane films were prepared on Si substrates. The resulting anionic surface was used to electrostatically adsorb positively charged proteins, such as horse heart cytchrome c. The formation of the sulfonated silane films was supported by XPS measurements, contact angle measurements, and ellipsometry measurements. The nature of the electrostatic adsorption of protein molecules and the protein film structure were investigated using a variety of surface spectroscopic techniques.

BI-TuP3 Adsorption Studies of Barnacle Cement Proteins from Balanus Improvisus*, **K. Mjorn**, F. Hook, H. Elwing,* Goteborg University, Sweden

Marine specimens such as barnacles and mussels anchor themselves to solid surfaces with biological glues that are curable under water. The glue used by barnacles is called cement, which is a clear proteinous liquid. When a barnacle is dislodged from a surface under certain conditions, such cement is secreted. The adsorption of fresh cement from the barnacle Balanus improvisus without prior purification has been studied on an electrically inert non-polar methylterminated thiolated gold surface and polar gold surface by a combined use of Surface Plasmon Resonance (SPR) technique and an extended version of Quartz Crystal Microbalance (QCM-D) technique. With SPR, which is an optical surface sensitive method, we can determine the adsorbed amount of protein at the surface due to the difference in refractive index between water and the protein. With QCM-D, an acoustic method, we can determine the degree of bound water in the protein layer and the structural flexibility of the proteins. The adsorbed mass was almost twice as great for the hydrophilic gold surface compared to the mass adsorbed on the hydrophobic surface showed with SPR. The amount coupled water did not differ in a great extent between the two surfaces. This indicates that the flexibility and the amount adsorbed water did not vary much with the chemistry of the surface, in contrast to the mussel adhesive protein, Mepf-1, showed by C. Fant et al.@footnote 1@ The behavior of the cement monolayer could then be followed with these two methods when the buffer conditions where changed, e.g. ionic strength and pH. The influence of this was also followed with 2D SDS-PAGE, where the separation of fresh cement was compared to treated cement. How and at which circumstances the cement is cured is under investigation. @FootnoteText@ @footnote 1@C. Fant, K. Mjorn, H. Elwing and F. Hook, Adsorption behavior and enzymatic induced cross-linking of mussel adhesive protein (submitted).

BI-TuP4 Soft X-ray Spectromicroscopy Studies of Protein-Polymer Interactions*, **A.P. Hitchcock**, T. Tyliszczak, Y.M. Heng, R. Cornelius, J.L. Brash,* McMaster University, Canada*; H.W. Ade,* North Carolina State University

Soft X-ray microscopy and micro-spectroscopy has considerable potential for characterizing the interaction of biological molecules with the surfaces of polymers used for biomaterials applications such as blood contact. We are exploring the use of scanning transmission X-ray microscopy (STXM) and various surface-sensitive X-ray microscopies - photoelectron emission microscopy (PEEM), scanning photoelectron microscopy (SPEM), and electron yield detection in STXM - for characterizing phase segregation at surfaces of polymers used for biomaterials applications, and for investigating specificity of cell and protein interactions with polymer surfaces. Transmission mode (STXM) has been used to study multilayer albumin adsorption on a polyurethane thin film which had micron-scale phase segregation. C 1s and N 1s STXM images and spectra recorded before and after protein exposure demonstrate that C 1s absorption spectroscopy differentiates protein, hard segment (urea), and soft segment (polyether) polyurethane signals and can locate proteins relative to an underlying phase segregated polymer. The strong C 1s -> @pi@*(C=O) excitation at 288.3 eV was found to be sufficiently well separated from the spectral features of the underlying polyurethane that considerable sensitivity to protein is achieved. The results clearly demonstrate that NEXAFS microscopy is relevant to biomaterials problems and that spatial segregation of protein does occur on phase separated polymers. Results to date suggest that albumin prefers the aromatic hard segment rather than the aliphatic soft segment regions of polyurethanes. The status of efforts to develop surface sensitive detection using total electron yield in STXM will also be discussed. 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-TuP5 A Circulating Flow Surface Plasmon Resonance System for Measuring Protein-Vesicle Binding Affinities*, **J. Shumaker-Parry**, L.S. Jung, M.H. Gelb, C.T. Campbell,* University of Washington

We have developed a circulating flow surface plasmon resonance (SPR) system for measuring equilibrium binding of proteins to surface-bound vesicles. Traditional methods for measuring interfacial binding of proteins to membranes often require the use of a non-physiological reporter group such as a tryptophan residue. The addition of a tryptophan has been shown to perturb binding in some cases. The fluorescence-based methods also lack the sensitivity to measure high binding affinities (K@sub d@ < 10@super-7@M). Other methods that rely on centrifugation are plagued by protein loss through non-specific adsorption on tube surfaces. Our circulating flow SPR system measures equilibrium binding constants rapidly without a spectral probe and can be used to quantify values of K@sub d@ down to 10@super -10@M. The sensing surface contains a high density of vesicles immobilized via biotinylated lipids that bind to biotin sites in a streptavidin monolayer. Fluorescence studies using dye-filled vesicles show that the vesicles remain intact when attached to the surface. We have used the surface-bound vesicles to measure K@sub d@ values for phospholipase A@sub 2@ with phospholipid vesicles. A circulating flow system is used to introduce the protein to the vesicle surface and the protein concentration can be adjusted by adding protein or buffer to a reservoir. A binding isotherm is generated by performing equilibrium titrations and is used to obtain the K@sub d@ value directly without the need to fit association and dissociation rate curves. We have shown that vesicles provide a more biologically relevant surface for measuring binding affinities than planar hybrid bilayer membranes.

BI-TuP6 Adsorption Behaviour and Enzymatic Induced Cross-linking of the Mussel Adhesive Protein, Mefp-1*, **C. Fant**, H. Elwing, F. Hook,* Goteborg University, Sweden

The blue mussel produces a family of 3, 4-dihydroxyphenylalanine (DOPA) containing proteins that allow the organisms to attach themselves to solid surfaces with high adhesive strength. We have studied the adsorption behaviour of the mussel adhesive protein, mefp-1, to a non-polar CH@sub 3@-terminated thiolated gold surface and to a polar silicone dioxide (SiO@sub 2@) surface. Cross-linking of these monolayers was induced by catechol oxidase, which catalyses the transformation of DOPA to a highly reactive o-quinone participating in cross-linking. The adsorption and the cross-linking of mefp-1 was studied with respect to changes in the mass and viscoelastic properties of the protein adlayer. This has been possible by combined use of the Surface Plasmon Resonance (SPR) and an extended version of the Quarts Crystal Micro Balance (QCM-D@super TM@). The SPR response are proportional to the adsorbed mass (m). QCM-D measures change in mass uptake as a change in frequency (f) of a piezo electric quartz crystal. The change in frequency is proportional to the adsorbed mass including trapped water. In addition, the QCM-D technique allows simultaneous measurement of the energy dissipation (D) related to the rigidity/viscoelasticity of the adlayer. The results suggest that the protein layer formed on the polar surface is rigidly attached. In contrast, the layer formed on the non-polar surface is flexible, and it contains a large amount of bound water. Upon cross-linking, the dissipation decreased more on the non-polar surface compared to the hydrophilic surface. This demonstrates that the combination of these techniques provides unique information with respect to rigidity and water content of the adsorbed protein. The combination of these two techniques also make it possible to study the cross-linking of mefp-1, which is important knowledge for the development of a medical glue.

BI-TuP7 Thin Films of Functionalized Poly(Ethylene Gylcol) for the Specific Attachment of Proteins*, S.N. Xia, H.B. Lu, C.T. Campbell, D.G. Castner,* University of Washington

The formation of ultrathin monolayers (10-30 angstroms thickness) of functionalized poly(ethylene gylcol) (PEG) oligomers and PEG-grafted siloxane polymers on gold surfaces has been investigated using x-ray photelectron spectrsocopy (XPS), static time of flight secondary ion mass spectromety (ToF SIMS), and surface plasmon resonance (SPR). PEG chains (MW 2000 to 5000) with an orthopyridyl-disulfide (OPSS) terminal group could be directly attached to a gold surface via formation of a gold-thiolate bond. By varying the type of terminal group at the other end of the PEG chain, the PEG monolayer can inhibit protein adsorption (OCH3), selectively attach proteins with surface cysteines (OPSS) through the formation of disulfide bonds, or selectively attach proteins with surface lysines (N-hydroxysuncciminide, NHS) through the formation of amide bonds. PEG monolayers that inhibit protein adsorption can also be formed from adsorption of siloxane polymer chains grafted with both methoxy-terminated ethylene gylcol and dialkyl disulfide side chains onto gold surfaces. The ability of the polymeric monolayers to specifically attach proteins with suface lysines was accomplished by replacing some of the methoxy-terminated PEG side chains with NHS-terminated PEG side chains.

BI-TuP8 A Novel Method for Characterization of Cell Surface Interactions*, S. Kihlman,* Chalmers University of Technology, Sweden*; C. Fredriksson, M. Rodahl,* Q-Sense AB, Sweden*; D.M. Steel,* Göteborg University, Sweden*; B. Kasemo,* Chalmers University of Technology, Sweden

A real-time in vitro technique to probe cell-surface interactions at biomaterial interfaces (e.g., contact surface, adhesion proteins, membrane and cytoskeleton modifications of the cell), would be very useful. In this study, we have explored the potential of a new method to characterize cell-surface interactions in liquid environments by dynamically monitoring the Quartz Crystal Microbalance (QCM) response due to adhering cells. The method is based on a new technique of simultaneously extracting resonant frequency and dissipation factor of the QCM. This is called QCM-D. It has here been applied to study the adhesion process of Chinese hamster ovary cells to polystyrene surfaces in serum-containing and serum-free environment at 37°C. The results show that: (i) adhesion of small colonies of a few hundred cells can readily be detected and characterized using the QCM-D technique, and (ii) the method of combining QCM data from changes in resonant frequency and dissipation factor gives new, relevant information about the character of the cell adhesion on surfaces and appears to be sensitive to properties of the surface (such as wettability) as well as the presence of serum-proteins on the surface.

BI-TuP9 The Role of Angiogenesis at Biomaterial Interfaces*, P.C. Stephans,* University of Washington*; R.B. Vernon, E.H. Sage,* Hope Heart Institute*; P.S. Stayton,* University of Washington

When a biomaterial is implanted, a relatively avascular fibrotic layer forms around the device. For devices such as sensors, this can inhibit the proper function of the device because the sensor only samples the microenvironment of the capsule. However, if the vascularity of the tissue adjacent to the device is increased, then the sensor can continue sampling a more representative environment. This problem has led to an interest in angiogenesis, the growth of new blood vessels from an existing vasculature, and how it is altered by various material properties. We are studying three material factors that may affect angiogenesis. The first, porosity, is based upon previous in vivo work that demonstrated a correlation between porosity and the number of vascular structures located close to the material. The second is coating the material with molecules, such as extracellular or matrix proteins. For example, we are currently immobilizing a peptide from SPARC that has shown angiogenic activity in vivo. The third factor is the release of soluble agents in the context of a material. Various soluble factors have been identified that are angiogenic, but now we can study the factor release from a material to determine if the angiogenic response can be stimulated within the material. To facilitate these studies, we are developing in vitro assays to study angiogenesis in the context of a biomaterial. For example, we have developed an assay to measure migration, a crucial step in angiogenesis. A teflon fence is used to grow endothelial cells to confluence in a well-defined area on the material. Once the fence is removed, the migration on various surfaces can be measured. The macrophage, a key player in angiogenesis, can also be incorporated into the assay to determine the effect of cytokine secretion on the endothelial cells. By studying the materials with these assays, we hope to gain a better understanding of the cell-material interactions that guide angiogenesis.

BI-TuP10 A Biosensor for In Vitro Monitoring of Cancer Cell Adhesion Behaviour*, G. Nimeri,* Gothenburg University, Sweden*; C. Fredriksson,* Q-sense AB, Sweden*; R. Hultborn, H. Elwing,* Gothenburg University, Sweden

A quartz crystal microbalance and dissipation (QCM-D) sensor, allowing simultaneous resonant frequency (f) and energy dissipation (D) measurements, was used to monitor cancer cell adhesion behaviour (attachment, spreading, and death) in vitro. This method is a mechanical sensor based on a minute (1nm) oscillation in the ultrasound frequency range. By measuring changes in f, the technique can be used to monitor the contact area of the cells with the substrate. Changes in D, which reflect energy losses as a result of friction in the system, provide information related to the internal structure (e.g., stiffness of the cytoskeleton). These two parameters offer new real time information regarding the status of cultured cells in vitro without interruption. The QCM-D signals were monitored for FADU cancer cells (human carcinoma squamous cells) for 8-24 hours. Cells were injected into a specially designed measurement chamber, filled with a minimal essential buffer and kept at 37 degrees C. The deposition and consecutive behaviour on the sensor surface, pre-coated with a tissue culture quality polystyrene overlayer, was then followed. Cell numbers from a few thousand up to a hundred thousand cells on a 1 cm2 surface were studied. The results show that the cells adhere and form a settled layer on the surface with relatively stable baselines in f and D after 4-8 hours. These baseline values indicate that a cultured layer of cells would provide contributions in f and D which can be monitored e.g., during cell growth or treatment. Preliminary results on the adhesion behaviour of non-treated and cells irradiated with 4 Gy (normal tumor treatment) show that the signals are distinctly different. The indications of differences in behaviour are considerably earlier than current methods based on growth rates (DNA staining etc).

BI-TuP11 The Effects of Surface Chemistry and Adsorbed Proteins on Monocyte/Macrophage Adhesion to Surfaces*, M. Shen, T.A. Horbett, Y.V. Pan, B.D. Ratner, K.D. Hauch,* University of Washington

Adherent macrophages play a central role in inflammatory responses to implanted biomaterials. Human monocyte adhesion to surfaces was therefore studied to determine the effects of surface chemistry, adsorbed proteins, and adhesion time. The surface chemistry of a series of commercially available modified polystyrene (PS) surfaces, fluorinated ethylene-propylene polymer (FEP), and plasma-polymerized-tetraglyme (PPT) coated FEP was analyzed by ESCA. The surfaces were preadsorbed with plasma, serum, fibrinogen, fibronectin, or albumin. Human monocytes in 10% serum were allowed to adhere to the surfaces for 2 hours or 1 day. Adhesion was measured by an LDH method. After 2 hours, monocytes adhered to most surfaces under all conditions examined. Adhesion was greater on charged hydrophilic TCPS, Plastek C, or Primaria than on hydrophobic PS, Plastek A, Plastek B, or FEP. Adhesion was lowest on uncharged hydrophilic PPT-coated FEP or Costar's Ultra Low Attachment hydrogel, which were also shown to resist fibrinogen adsorption. Monocyte adhesion was greater on surfaces preadsorbed with fibrinogen or fibronectin than on surfaces preadsorbed with albumin. However, 2-hour adhesion to surfaces preadsorbed with serum was similar to surfaces preadsorbed with plasma, despite the lack of fibrinogen. Preadsorption of dilute plasma or serum increased adhesion to TCPS but did not increase adhesion to PS. After 1 day, monocyte adhesion decreased and was lowest to surfaces without preadsorbed proteins. One-day adhesion was greater on plasma than on serum preadsorbed surfaces and was much greater on fibrinogen or fibronectin than on albumin preadsorbed surfaces. Overall, monocytes adhered to all surfaces and preadsorbed fibrinogen and fibronectin significantly promoted monocyte adhesion. Non-fouling surfaces that minimize protein adsorption may minimize overall macrophage adhesion and activation.

BI-TuP12 Human Monocyte/Macrophage Adhesion to Biomaterials Surfaces*, J. Shan, T.A. Horbett, C.M. Giachelli,* University of Washington

The biocompatibility of synthetic implants is thought to be related to their attractiveness to monocyte/macrophages. The hydrophobicity and protein adsorption capabilities of an implant surface are believed to influence the adhesion of monocytes and macro phages. Therefore, a range of materials varying widely in hydrophobicity and protein adsorption characteristics were evaluated for monocyte/macrophage adhesion in vitro. Freshly isolated human peripheral blood monocytes were cultured on surfaces in the p r esence of autologous serum from 2 hour up to 8 days. The surfaces includes polystyrene (PS), tissue culture treated polystyrene(TCPS), human fibrinogen (Fbg) preadsorbed to PS (Fbg-PS), BSA preadsorbed PS (BSA-PS), plasma polymerized hexaflurocarbon (C 3F6) coated PS, plasma polymerized triglyme coated PS(triglyme), fluoro-ethylene-propylene (FEP) copolymer, and plasma polymerized tetraglyme coated FEP(PEO-FEP). Monocyte adhesion was determined by measuring the LDH activity of lysates. Of these surfaces, t he most hydrophobic is C3F6 coated PS, the most hydrophilic surface was PEO-FEP, which had less than 5ng/cm2 adsorption of Fbg from 1% human plasma. Adhesion to most PS based surfaces was similar for periods up to 24 hours. However, monocyte adhesion to T CPS was much lower by 24 hours. Monocyte adhesion to PEO-FEP at earlier hours was about 1/2 to 1/3 of the level achieved on PS and FEP, respectively. After the 8 day period, macrophage adhesion to the surfaces ranged from none on TCPS and Fbg-PS, low on B SA-PS, to significantly higher on PS, C3F6, triglyme and PEO-FEP. Adhesion to PEO-FEP after the 8-day period was similar to that on PS, C3F6, and triglyme, however macrophage morphologies differed among surfaces. Possible explanations (including non-protein mediated mechanisms) for monocyte/macrophage adhesion to PEO-film will be included in the poster presentation.

**BI-TuP13 Adhesion of Endothelial Cells to Patterned OTS Surfaces*, S.R. Webb*, *T.B. Boland, D.R. Weinbrenner,* Clemson University

Thromboresistance is necessary for a biomaterial in vascular applications to maintain proper function. One approach to thromboresistance is to line the interior wall of artificial vascular grafts with endothelial cells.This study examines the effects of surface chemistry and adhesion of endothelial cell membranes to proteins. Hence, understanding these two factors will facilitate applications to reduce thrombogenesis. Cell response to patterned materials was examined by employing highly organized monolayers of self-assembled octadecyltrichlorosilane (OTS) on a silicon wafers. Pure OTS monolayers are poor substrates for cell growth, most likely because of the denaturing of serum proteins near the surfaces. The OTS surfaces were exposed to an electron beam, which selectively oxidized the organic film, creating a variety of oxygenated species at the surface. The monolayers and the patterned surfaces were analyzed by ellipsometry, water contact angle, electron spectroscopy for chemical analysis (ESCA) and AFM. Bovine heart endothelial cells were cultured. Cells were inoculated at 1 x 106 cfu/mL and cultured in twelve well plates in the presence of pure and patterned OTS surfaces. To insure the cells were not toxic to the OTS surfaces three cytotoxicity test were performed. The first was a live dead assay in which calcein green was used to determine if the cells were viable. The second test was MTS to determine if the cells were proliferating. The last test to determine how cytotoxic the surfaces were to the cell was BCA or total protein test. All three tests proved that the patterned surface was not toxic to the cells. The attachment, spreading and growth of the cells on the surfaces will also be presented. The cell spreading on the etched surfaces suggests that the cells may be able to attach more firmly to the extracellular proteins on the etched pattern. The results from this cell growth study will aid in designing micro-patterned surfaces for cell-based biosensors.

**BI-TuP14 Microcontact Printing of Protein Patterns to Direct Cellular Response*, T.C. McDevitt*, *M.D. Garrison, T.R. Kyriakides, M. Scatena, P. Bornstein, C.M. Giachelli, P.S. Stayton,* University of Washington

In order to control the cellular response at a biomaterials interface, we are applying micropatterning techniques to spatially arrange extracellular matrix (ECM) ligands on surfaces. Cell function has previously been related to cell shape and cytoskeletal architecture, thus we are investigating how microcontact printing of proteins can be used to modulate these parameters. Various combinations of ECM proteins can be patterned to create heterogeneous, ordered surfaces that selectively promote cell adhesion, spreading, and intracellular signaling events. Designated adhesive and non-adhesive regions are dictated by the choice of particular ECM proteins which possess these characteristics and cell attachment is confined by the features of the micropatterning. Our aim is to use micropatterning as a tool to recreate an ordered, complex surface that more accurately resembles the true ECM, stimulates a specific and desirable cellular response, and thus induces a more favorable interaction with the biomaterial.

**BI-TuP15 Surface Functionalization Strategies for Miniature Multichannel Biosensing*, H.B. Lu*, *J. Homola, C.T. Campbell, B.D. Ratner, S.S. Yee,* University of Washington

Biosensor development has advanced towards highly integrated, multichannel array configurations with more detection power and faster speed. Robust surface functionalization methods for immobilizing sensing molecules and making non-fouling surfaces are needed. Also, precise spatial control of surface functionalization is valuable. In this presentation, various surface functionalization methods including orthogonal self-assembly (OSA), masked plasma polymerization and protein contact printing are introduced. The potential of these methods for precisely immobilizing sensing biomolecules to specific surface regions, or creating a non-fouling area using passivation molecules, is discussed. We used a dual-channel surface plasmon resonance (SPR) sensor with a thin tantalum oxide (Ta2O5) overlayer configuration for demonstrating the feasibility of these surface functionalization methods, as well as for further developing a miniaturized multichannel biosensor. The high refractive index dielectric Ta2O5 overlayer covers part of the gold surface to excite part of the incident light in a higher wavelength and thus produce a second SPR dip besides the original gold SPR dip. To use this second SPR dip as an internal reference channel, the surface functionalization methods were used to deliver biosensing molecules (e.g. antibodies) or passivation molecules (e.g. oligo(ethylene glycol) or bovine serum albumin) to the gold or the Ta2O5 surface respectively. The optical nature of such an SPR sensor configuration requires precise delivery of molecules to these two surface regions in order to separate signal from the two channels. Therefore, it provides an excellent tool for demonstrating the spatial control ability of the surface functionalization methods used. The surface functionalization strategies described in this paper should have general applicability for developing miniaturized multichannel biosensors in other formats as well.

**BI-TuP16 Kinetics of Vesicle Adhesion and Fusion*, K. Glasmästar*, *F. Höök, C.A. Keller,* Chalmers University of Technology and Göteborg University, Sweden*; V.P. Zhdanov,* Chalmers Univ. of Tech., Göteborg Univ., Sweden and Institute of Catalysis, Novosibirsk, Russia, Sweden*; B. Kasemo,* Chalmers University of Technology and Göteborg University, Sweden

Vesicle adhesion and fusion are essential in many cellular processes and in the formation of supported membranes. Because of their similarity to natural membranes, they play an important role in the development of biosensors and in model studies of membrane-mediated processes. We have studied the kinetics of adsorption of small unilamellar lipid vesicles on carefully prepared SiO@sub 2@ surfaces and their subsequent fusion to form a lipid bilayer, using surface plasmon resonance (SPR) and a new quartz crystal microbalance (QCM-D) technique. With the latter the energy dissipation (D) and the resonance frequency (f) of the QCM oscillator are measured. The lipid mass adsorbed at the surface and the mass of water trapped by the adsorbed layer are measured as changes in f. The SPR technique is only sensitive to the amount of lipid adsorbed. Since one of the primary differences between lipids adsorbed as vesicles or as a bilayer is the water trapped within and between the vesicles, the combination of the two techniques provides a detailed picture of how a lipid bilayer forms on the SiO@sub 2@ surface. In addition the two types of adsorption have very different viscoelastic properties, which are reflected in the D factor. The formation of a lipid bilayer on a SiO@sub 2@ surface is a two-stage process. First a layer of intact vesicles adsorbs on the surface. Then at a sufficiently high surface concentration the vesicles begin to break and form a fluid bilayer. From detailed QCM-D and SPR measurements at different vesicle concentrations in the liquid phase, we find that (i) the adsorption is irreversible, (ii) it is rate limited by bulk diffusion, (iii) vesicle to bilayer transformation starts at a critical surface coverage, after which (iv) further adsorption from the bulk phase drives the vesicle to bilayer transformation. The kinetics of these events is further elucidated by Monte Carlo simulations, employing different mechanistic models for the kinetics.

BI-TuP17 Thiopeptide-Tethered Lipid Bilayers for the Incorporation of the Enzyme Complex Cytochrome c Oxidase*, H.D. Lauer*, Max-Planck-Institut for Polymer Research, Germany*; E.K. Schmidt,* Lab. for Exotic Nanomaterials Frontier Research Program, Japan*; R. Naumann,* Max-Planck-Institut for Polymer Research, Germany*; A. Offenhäusser,* Max-Planck-Institut for Polymer Reseach, Germany*; W. Knoll,* Max-Planck-Institut for Polymer Research, Germany

Lipid bilayers form the basic structure of biological membrane due to which membrane proteins are able to carry out their specific functions. Membrane proteins have precisely designed moving parts whose mechanical actions are coupled to chemical events. This coupling of chemistry and movement is the reason why membrane proteins play the predominant role in most biological processes. Without a better understanding how proteins operate, it is very difficult to apreciate cell biology. Therefore in the last few years a number of model systems have been developed to create a biomimetic system. To retain the functionality of an incorporated membrane protein, the lipid bilayer should be fluid and the membrane/protein-complex has to be to some extent spatially decoupled from the substrate. Without this decoupling from the surface, the protein denatures. A number of spacers are well known to decouple the membrane/protein-complex from the gold substrate and preserve a thin water reservoir between lipid and the gold.@footnote 1, 2, 3@ We present here a biomimetic system utilising thiopeptides as spacer molecules chemisorbed onto a gold surface and covalently attached to lipid layer.@footnote 4@ This system is used to incorporate the membrane protein cytochrome c oxidase, a key enzyme in the cell respiration. Optical and electrochemical characterisation methods are used to obtain more information about the architecture and the operation of the membrane/protein-complex. @FootnoteText@ @footnote 1@ Cornell, B.A. et al., Nature, 387, 1997, 580 @footnote 2@ Vogel, H. et al., J. Phys. Chem., 99, 1995, 1038 @footnote 3@ Evans, S.D. et al., Langmuir, 13, 1997, 751 @footnote 4@ Naumann, R., et al., Angew. Chem., 107, 1995, 2168.

BI-TuP18 Functionalized Glycolipids for Model Biomembrane*, **S. Schiller**,* Max-Planck-Institut for Polymer Research, Germany*; H. Kunz,* University of Mainz, Germany*; W. Knoll,* Max-Planck-Institut for Polymer Research, Germany

Fluid Model Biomembranes are important tools for general investigations of membrane properties and have many potential applications in the pharmaceutical industry e.g. for analyte screening using competitive immuno assays with membrane-integral receptors. The most advanced of these systems are tethered lipid bilayer membranes (tBLMs) on gold or silicon. tBLMs developed so far often show poor electrical properties compared to BLMs. Some systems insufficiently decouple the lipid bilayer from the surface and do not provide optimal tether properties in terms of hydrophilicity of the submembrane and stable membrane support, which is necessary for the incorporation of membrane proteins. An alternative route uses functionalized carbohydates as tether molecules to meet some of these requirements. Several carbohydrate systems are already under investigation, polysaccharides, especially dextran, cellulose and agar are used to provide a hydrophilic, soft and gel like support. Regio- and stereospecific manipulations in small and defined areas are difficult in such large polymer systems. We therefore focus on small oligosaccharides and their functionalized derivatives and the synthesis of a complex multicomponent system with specific lateral spacer molecules and several glycolipid tether sytems. Important components are glycolipids functionalized with anchor groups for surface attachment and spacer saccharides. The possibility to introduce side functionalities to multifunctional saccharides opens a wide range of variations, for example the functionlization with fluorescent probes at different positions along the tether chain or variation of physical properties by varying side groups. The approach we present here consists of the use of several saccharides and different lipids to learn more about the fundamental properties of these systems. Further research will be the synthesis of the complex system described above and the challenging study of complex membrane processes.

BI-TuP19 Force Differentiation Assay: A New Approach Sensing*, **M. Natesan**,* GeoCenters*; C. Yanavich,* Nova Research*; S. Metzger,* Geocenters*; G.U. Lee,* Naval Research Laboratory

Biomolecular interactions have recently been measured at the single molecule scale using microscopic techniques such as atomic force microscopy, optical tweezers and micropipettes. The force required to rupture a specific interaction has been found to be a characteristic of the structure of the molecular interaction and the rate at which it is stressed. We have used these insights to develop a new approach to molecular detection based on sensing force. Force detection has two advantages, it has single molecule sensitivity and the magnitude of the force can be used to differentiate specific from nonspecific interactions. We will describe two force based diagnostic techniques that apply a magnetically derived force to an antibody-antigen sandwich using a micron size particle.

BI-TuP20 Solid Supported Lipid Bilayers by Fusion of Mixed Thiolipid/Lipid Vesicles onto Gold*, **H. Wieder**, S. Lingler,* Max-Planck-Institute for Polymer Research, Germany*; J. Mack,* Institute for Organic Chemistry, Germany*; A. Offenhäusser,* Max-Planck-Institute for Polymer Reseach, Germany

Recently, planar solid supported lipid membranes have become a frequently used model system for biological membranes. Their big advantage to other model systems is the relatively high stability to mechanical and electrochemical stress in addition to the accessibility by a variety of surface sensitive techniques. These features make them an interesting system for biosensing applications. In this work supported lipid mono- and bilayers tethered to Au-electrodes by thiolipids are being investigated using surface plasmon resonance spectroscopy (SPR), impedance spectroscopy (IS), cyclic voltammetry (CV), reductive desorption and contact angle measurements. Following work on hybrid bilayer membranes,@footnote 1@ we are now looking at systems with and without laterally diluted hydrophilic spacers of different length to provide a hydrophilic reservoir between membrane and support. The dependence of the membrane properties on different parameters in the preparation by self-assembly, LB-techniques and vesicle fusion are being investigated. Into the membranes noted above transmembrane proteins are reconstituted and checked for their functional activity. @FootnoteText@ @footnote 1@Lingler S., Rubinstein I., Knoll W., Offenhäusser A. (1997) Fusion of Small Unilamellar Lipid Vesicles to Alkanethiol and Thiolipid Self-Assembled Monolayers on Gold, Langmuir 13, 7085-7091.

BI-TuP21 Incorporation of Membrane Proteins into Lipid Bilayers Supported on a SiO@sub 2@-surface.*, **A. Persson**, F. Höök, J Rydström, B. Kasemo,* Chalmers Univ. of Tech. and Göteborg Univ., Sweden

Transmembrane proteins are difficult to study in their native state, since detergents are used for the solubilization of transmembrane proteins, which might influence the protein properties and function. One way to circumvent this is to incorporate the proteins into lipid membranes deposited on solid supports. The focus of this project is to combine spontaneous formation of lipid membranes on solid supports, known to occur on SiO@sub 2@, with incorporation of transmembrane proteins. Understanding and mastering of this process has important implications for the development of biosensors and biomaterials, for investigations of the respiratory chain, studies of the photosynthesis, and in neurobiology. Small unilammellar vesicles (SUV's) form a lipid bilayer on hydrophilic SiO@sub 2@-surfaces.@footnote 1@ This process is most likely a two-stage process, where initially intact vesicles adsorb at the surface at low coverages. When a certain surface-concentration of SUV's is reached, the vesicles break and form a fluid bilayer. The protein containing SUV's studied in this work seem to behave in the same way. The SUV's were prepared by sonicating different phospholipids in buffer, and the proteins were incorporated with detergent. The vesicle and protein adsorption is studied with a new QCM-D technique where the frequency shift (mass adsorbed on the surface) and the energy dissipation shift (reflecting the viscoelastic properties of the overlayer) are measured simultaneously.@footnote 2@ The presence of the proteins in the supported bilayer is, after deposition, directly measured using the QCM-D technique, combined with a secondary process using specific monoclonal antibodies to the membrane bound proteins. The preparation procedures and the first results are presented. @FootnoteText@ @footnote 1@Keller, C. A., et al. 1998. Biophys. J. Vol 75 p.1397 @footnote 2@Rhodahl, M., et al. 1995. Rev. Sci.Instrum. Vol 66 p.3924.

BI-TuP22 A Dissimilatoric Nitrate Reductase as a Signal Transducer in a Tethered Membrane FET Architecture*, H. Borcherding, **Th. Hettmann**, S. Diekmann, P. Steinruecke,* IMB Jena e.V., Germany

Nitrate reductase is a key enzyme in the anaerobic denitrification of nitrate to elementary nitrogen. Nitrate is reduced to nitrite in the catalytical @alpha@-subunit of the enzyme. The dissimilatoric enzyme from Pseudmonas stutzeri also comprises a membrane-integral @gamma@-subunit which is involved in the transfer of electrons from the the bacterial quinole pool to the site of nitrate reduction. This makes the enzyme a valuable functional unit for reconstitution in lipid bilayers. We developed a suitable purification protocol for nitrate reductase from Ps. stutzeri . The enzyme is reconstituted in phospholipid vesicles which are used for the reconstitution of the enzyme in a tethered bilayer covering the gate of a field effect transistor. By generation of a nitrate-specific transmembrane potential, it should be possible to design a nitrate-specific FET biosensor. Data will be given on the suitability of our approach to create a new type of biosensor.

BI-TuP23 On Compressional Wave Velocity in Animal Bone by Compensated Ultrasonic Timer Technique (CUTT)*, **S. Mohiuddin**,* King Saud University, Saudi Arabia

Ultrasonic propagation properties play a vital role, as they throw light on molecular architecture and cellular assembly of the living system, in understanding the physiological reality of the system which is involved in the life processes. The present investigation on compressional wave velocity of cancellous bone (Scapula and rib) and compact bone (femur) by adopting compensated ultrasonic timer technique, reveals that in cancellous bone tissue (scapula and rib), ultrasonic compressional wave velocity is the same, but it is relatively more than that of compact bone (femur). Considering the values of compressional wave velocity obtained for scapula, rib and femur, when measured at different places of the same sample along its axis, there exit no definite relations between the parameters related to the composition the bone and the parameters concerned with the propagating ultrasonic wave in the tissue. The compressional wave velocity in bovine scapula, rib and femur bones is more than those reported for soft tissues and hard calcified derivatives of integuments. It is interesting to note that the velocity in the bone is high when compared to other tissue of the same animal.

Surface Science Division
Room 4C - Session SS-TuP
Poster Session

SS-TuP1 Vacuum TPD from Traditional and Nano-fabricated Pt/Alumina Model Catalysts*, **E. Fridell**, T.R. Linderoth, B. Kasemo,* Chalmers University, Sweden

Temperature Programmed Desorption (TPD) is a valuable method to identify adsorbed species and investigate desorption kinetics. The usual method of performing TPD for (practical) catalyst samples is in a flow reactor under inert gas flow. The interpretation of the resulting spectra is hampered by complications associated with thermal gradients in the samples, re-adsorption of the desorbed species, gas phase transport under viscous flow conditions, etc.To remedy these problems, we have constructed an equipment allowing UHV-TPD from both model samples and "real" catalysts: The samples can be pre-treated at atmospheric pressures and high temperatures in a reactor cell mounted onto a UHV system. They are then exposed to the adsorbing gas before being translated to a position in front of a mass spectrometer for TPD in vacuum. The catalyst washcoat is applied directly onto, e.g., a metal foil which can be cooled or heated resistively providing precise temperature control. The equipment is intended primarily for catalysts made by traditional wet-deposition, but also for new "nano-fabricated" samples. To produce the latter, several methods are employed, for example we use colloidal particles adsorbed onto a surface as masks for sputtering of vacuum deposited metal/oxide films. After removing the colloidals the resulting 2D model catalysts consist, e.g., of Pt particles of uniform sizes and with controlled spatial separations on an alumina surface. In this presentation the equipment will be described and results of just initiated measurements concerning CO/oxygen adsorption on Pt/alumina catalysts will be presented.

SS-TuP2 Growth Mode of Au on SiO@sub 2@ Ultrathin Film*, **K. Luo**,* Texas A&M University*; D.Y. Kim,* Hallym University, Korea*; D.W. Goodman,* Texas A&M University

Au clusters supported on SiO@sub 2@/Mo(110) have been studied by x-ray photoemission spectroscopy(XPS), low energy ion scattering(LEIS), temperature programmed desorption(TPD) and low energy electron diffraction(LEED). At both 100 K and 300 K, the growth mode of Au at fractional monolayer coverages is quasi-two dimensional. With higher coverages, three dimensional growth of Au was found. No strong chemical interaction was observed between gold and silica. By annealing Au/SiO@sub 2@/Mo(110) to 1000 K, sintering of gold clusters was observed. The Au desorption activation energy was measured by temperature programmed desorption to be about 42 kcal/mol, lower than the sublimation energy of 90 kcal/mol for bulk gold.

SS-TuP3 Nucleation and Growth of Faceted Features on the Platinum Covered W(111) Surface*, **K. Pelhos**,* Rutgers, The State University of New Jersey*; J.B. Hannon, G.L. Kellogg,* Sandia National Laboratories*; T.E. Madey,* Rutgers, The State University of New Jersey

Low energy electron microscopy (LEEM) and scanning tunneling microscopy (STM) have been used to investigate the faceting of W(111) as induced by Pt. The atomically rough W(111) surface, when fully covered with a complete physical monolayer (1.7 x 10@super 15@ atoms/cm@super 2@) film of Pt and annealed to temperatures higher than ~750 K, experiences a significant morphological restructuring: the initially planar surface undergoes a faceting transition and forms three-sided pyramids with {211} faces. LEEM investigations show that when Pt is dosed onto the heated surface, the transition from planar to faceted structure proceeds through the nucleation and growth of spatially separated faceted regions starting at 2/3 physical monolayers coverage. STM reveals the atomic structure of the partially faceted surface, with large planar regions, dotted by clusters of pyramids of various sizes. On the other hand, when the initially planar sample is first completely covered with a physical monolayer of Pt and gradually heated, LEEM does not show any spatial separation in the faceting transition. STM observations of the initial stages of this transition show a continuous uniform roughening of the surface towards the faceted phase.

SS-TuP4 Adsorption of O@sub 2@ on Al(111) - No Evidence for "Hot Adatoms"*, M. Schmid, **P. Varga**,* Technische Universität Wien, Austria

Based on a scanning tunneling microscopy (STM) study,@footnote 1@ it has been suggested that adsorption of O@sub 2@ on Al(111) results in a high transient mobility of the two oxygen atoms created by dissociation of the oxygen molecule. It was suggested that these atoms move at least 80 Å apart before they come to rest at the surface.@footnote 1@ We have performed experiments under the same conditions. High-resolution STM images enable us to identify the features considered single O adatoms in ref. 1 as two O atoms in adjacent fcc hollow sites. We also find groups of three and four oxygen atoms, however. The dynamics of the O dimers point to an attractive interaction of O atoms in adjacent fcc hollow sites. These findings do not completely rule out the possibility of a large transient mobility and subsequent diffusion of individual O atoms, finally forming stable dimers. We consider it more likely, however, that only few O@sub 2@ molecules do not stay in adjacent hollow sites during adsorption and the single O adatoms created thereby diffuse until they coalesce with one of the dimers or larger O groups on the surface. With decreasing tunneling distance, Al atoms with three and two O neighbours appear as protrusions, explaining images with protrusions earlier attributed to single O adatoms. @FootnoteText@ @footnote 1@H. Brune et al., Phys. Rev. Lett. 68, 624 (1992); J. Chem. Phys. 99, 218 (1993).

SS-TuP5 Adsorption Dynamics of Oxygen on Al(111)*, **A.J. Komrowski**,* University of California, San Diego*; Y. Liu,* Syagen Technologies, Inc.*; A.C. Kummel,* University of California, San Diego

The interaction of oxygen with aluminum has become a prominent system in the study of metal oxidation. A previous study of Al(111) reacted with thermal O@sub 2@ at low coverages observed isolated features separated by >80 Angstroms which were attributed as dissociated O atoms.@footnote 1@ We have studied the oxidation of Al(111) using supersonic molecular beam techniques and scanning tunneling microscopy. The adsorption of monoenergetic O@sub 2@ on the Al(111) surface shows a change in the chemisorption site distribution (single reacted sites vs. doubles) with incident translational energy. We will contrast the O@sub 2@--Al(111) reaction against data from the reaction of supersonic oxygen atoms with Al(111) and compare the chemisorption results between activated and non-activated processes. @FootnoteText@ @footnote 1@ Brune, H. et. al. J. Chem. Phys. v99, 2128 (1993).

SS-TuP6 Water Dissociation on Boron-Doped Single Crystal Ni@sub3@(Al,Ti) (110) Surface*, **J. Wang**, B. Zhou, Y.W. Chung,* Northwestern University

Previous work demonstrated that water dissociates into hydrogen on Ni@sub3@(Al, Ti) (100) surfaces. There is clear evidence that this dissociation reaction results in the reduced ductility of many polycrystalline aluminum-based alloys in a moist environment. Ductility measurements further showed that addition of boron suppresses this moisture-induced embrittlement. 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 boron ion source, followed by low-temperature exposure to D@sub2@O and temperature-programmed desorption. Results indicated that water dissociates into atomic hydrogen on clean Ni@sub3@(Al, Ti) (110) boron-free surface, which was further verified by x-ray photoemission studies. This dissociation reaction is strongly suppressed by boron adsorption at a coverage of 0.5 monolayer. Auger studies on boron modified surfaces showed that boron is oxidized in this process. The chemical state of water was followed by x-ray photoemission. These studies indicated that addition of boron suppresses water dissociation into atomic hydrogen. By co-adsorption of D@sub2@O and oxygen on boron-modified Ni@sub3@(Al, Ti) (110) surfaces, the effect of oxygen was also investigated by temperature-programmed desorption. The significance of this observation will be discussed.

SS-TuP7 Ethene Adsorption on Cu(111), Cu@sub 3@Pt(111), CuPt@sub 3@(111), and Pt(111)*, **T. Pelster**,* Universität Bonn, Germany*; R. Linke,* Eindhoven University of Technology, The Netherlands*; J. Breitbach, A. Frey,* Universität Bonn, Germany*; M. Tanemura,* Nagoya Institute of Technology, Japan*; M. Grüne, R.-J. Linden, C. Becker, K. Wandelt,* Universität Bonn, Germany

The adsorption of ethene on Cu(111), Cu@sub 3@Pt(111), CuPt@sub 3@(111), and Pt(111) at 100K has been investigated using high resolution energy electron loss spectroscopy (HREELS), temperature programmed desorption (TPD), ultraviolet photoelectron spectroscopy (UPS), and work function change measurements. On Pt(111) ethene forms at 100K a well known di-@sigma@-complex, whereas on Cu(111) ethene adsorbs in a weakly bonded @pi@-complex which shows typical vibration spectra very similar to gaseous ethene. On Cu@sub 3@Pt(111) and CuPt@sub 3@(111) both species can be found, with higher intensity of the @pi@-complex on the Cu@sub 3@Pt(111) and the di-@sigma@-complex on the CuPt@sub 3@(111) surface, respectively. A full peak assignment in HREELS spectra gives a strong indication for a reduction of the C-C bond order of the di-@sigma@-species going from Cu@sub 3@Pt(111) to Pt(111). This can be attributed to an electronic effect due to the dilution of Pt by Cu. Both TPD and UPS support these results. Surprisingly, ethene does not dehydrogenate on the alloys when the surface is heated in contrast to ethene on Pt(111). This can be explained by the lack of appropriate sites on Cu@sub 3@Pt(111). On CuPt@sub 3@(111) the issue is more complex since on this surface such sites are available. On this surface the process might therefore be kinetically hindered.

SS-TuP8 HREELS and XPS Studies of Fe(C@sub 5@X@sub 5@)@sub 2@ / Ag(100) where X=H, D, or Me*, **C.M. Woodbridge**, D.L. Pugmire, M.A. Langell,* University of Nebraska, Lincoln

Although metallocenes show great potential as novel Chemical Vapor Deposition (CVD) source molecules, very little is known about how they bond to metal surfaces. Therefore, systematic investigation of ferrocene adsorption to different single crystal substrates are essential for understanding and controlling CVD processes involving metallocenes. We have used HREELS and XPS to study ferrocene, Fe(C@sub 5@H@sub 5@)@sub 2@, deuterated ferrocene, Fe(C@sub 5@D@sub 5@)@sub 2@, and its methylated derivative on Ag(100). HREELS was used to confirm the molecular nature of the adsorbed metallocene, determine the orientation and quantify interactions between ferrocene and the silver substrate. XPS was used to evaluate the chemical state of iron and carbon in the ferrocene films and to quantify the adsorbate surface concentration. Specific information about orientation and chemical shifts as a function of ferrocene exposure will also be presented.

SS-TuP9 Insertion Process of Conjugated Molecules into n-Alkanethiol Self-Assembled Monolayers on Au(111)*, **T. Ishida**,* JRCAT-NAIR and PRESTO-JST, Japan*; W. Mizutani,* JRCAT-NAIR, Japan*; U. Akiba,* Tokyo Institute of Technology, Japan*; N. Choi,* JRCAT-ATP, Japan*; M. Fujihira,* Tokyo Institute of Technology, Japan*; H. Tokumoto,* JRCAT-NAIR, Japan

Since conjugated molecules are a good candidate for the components of nanoscale devices, functions of organic molecules have been investigated in search of their potential applications. To analyze the property of such conjugated molecules, insertion of such a molecule into pre-assembled n-alkanethiol SAMs on Au(111) is attracted recently. We have investigated using STM insertion process of conjugated molecules, benzylmercaptane (BM), 4-biphenylmethanethiol (BP), and [1,1':4',1''-Terphenyl]-4-methanethiol (TP) into alkanethiol SAMs. These conjugated molecules were inserted into boundaries between structural domains of n-alkanethiol SAMs at the initial stage of insertion reaction. The insertion process rate increased with the number of phenyl rings of the conjugated molecule, i.e., the most of alkanethiols were replaced by BP and TP for 3-4 h and 2 h, respectively. On the other hand, BMs were inserted in the domain boundaries even after one day insertion reaction. These results suggested that the interaction energy difference between the conjugated molecules and alkanethiols strongly affected the insertion reaction.

SS-TuP10 Adsorption and Thermal Decomposition of 1,3-butadiene and 2-butyne on Ru(001)*, **M.J. Weiss**, C.J. Hagedorn, W.H. Weinberg,* University of California, Santa Barbara

The low temperature (80 K) molecular adsorption and subsequent thermal decomposition of 1,3-butadiene and 2-butyne are studied on Ru(001) using temperature programmed desorption and high resolution electron energy loss spectroscopy (HREELS). After heating to 300 K, the 1,3-butadiene decomposes to yield a (CH)@sub 4@ surface metallacycle. This result is particularly interesting in that the (CH)@sub 4@ species has been implicated as an intermediate in the production of 1,3-butadiene (and other molecules) during thiophene hydrodesulfurization. 2-butyne adsorbs at a coverage of 0.27 molecules for every surface ruthenium atom, a coverage which is equal to that observed for the adsorption of acetylene on this surface. The 2-butyne decomposes to yield surface hydrocarbon fragments whose HREEL spectra resemble those of vinylidene, acetylide, and methylidyne. Slight differences in the spectra, however, suggest that the fragments observed in the present work may actual be analogous species containing four carbon atoms.

SS-TuP11 A Study of Boron Effects on the Reaction of Co and SiGe at Various Temperatures*, **H.J. Huang**, K.M. Chen,* National Chiao Tung University, Taiwan, R.O.C.*; T.C. Chang, G.W. Huang, L.P. Chen,* National Nano Device Laboratory, Taiwan, R.O.C.*; C.Y. Chang,* National Chiao Tung University, Taiwan, R.O.C.

The boron effects on Co and SiGe interfacial reaction were studied with RTA from 500°C to 1000°C. The undoped and in-situ boron-doped strained Si@sub 0.91@Ge@sub 0.09@, Si@sub 0.85@Ge@sub 0.15@ layers were prepared at 550°C by ultra-high vacuum chemical vapor deposition system for silicidation. The resulting films were characterized by sheet resistance measurement, Auger electron spectroscopy, X-ray diffractometry, high resolution X-ray diffractometry, secondary ion mass spectroscopy, scanning electron microscopy, and transmission electron microscopy. Co(Si@sub 1-y@Ge@sub y@) cubic structure was formed from 500°C to 700°C RTA with different Ge content. For the boron-doped sample, Ge content (y = 0.064, 0.054) in Co(Si@sub 1-y@Ge@sub y@) was less than undoped sample (y= 0.12, 0.11) after 500°C RTA, which can be discovered by X-ray diffraction. This implied that boron atoms retarded the incorporation of Ge into the Co(Si@sub 1-y@Ge@sub y@) ternary phase. It also led to large piled-up of Ge at the reaction interface. On the other hand, according to the X-ray rocking curve, boron-doped sample led to less relaxation of strained SiGe layer. Furthermore, from sheet resistance measurement, the formation of CoSi@sub 2@ was a little slower in boron doped sample than in undoped sample. This may be due to the decrease of Co diffusivities, which was caused by the boron accumulation at the Co/SiGe reaction interface. At temperature above 800°C, CoSi@sub 2@ was formed and the underlying SiGe layer was almost totally consumed. From the AES and TEM analyses, Ge segregation to the surface and the CoSi@sub 2@ grain boundary was observed.

SS-TuP12 Vacancy Mediated Growth of Ga@sub 2@Se@sub 3@ Thin Films*, **Z. Qian**, Z. Dai, F.S. Ohuchi,* University of Washington*; K. Ueno, A. Koma,* University of Tokyo, Japan*; S. Meng, M.A. Olmstead,* University of Washington

Ga@sub 2@Se@sub 3@ thin films were grown on GaAs(100) and Si(111) substrates by molecular beam epitaxy (MBE). In spite of large differences in lattice and symmetry found in GaAs(100) and Si(111), reflection high energy electron diffraction (RHEED) showed that the Ga@sub 2@Se@sub 3@ thin films were epitaxially grown on both surfaces. Electronic structures were determined by ultraviolet photoelectron spectroscopy (UPS) and electron energy loss spectroscopy (EELS). For the Ga@sub 2@Se@sub 3@ thin films growth on GaAs(100) substrate, transmission electron microscopy (TEM) revealed that vacancies were distributed on one set of the [111] crystal planes of @alpha@-Ga@sub 2@Se@sub 3@ structure by forming a @sr@3x@sr@3 configuration, resulting in the formation of vacancy ordered @beta@-Ga@sub 2@Se@sub 3@ structure. In this structure, modulation periodicity along [110] crystal directions was three times larger than that of @alpha@-Ga@sub 2@Se@sub 3@, and the crystal structure was consistent to the model proposed by Lübbers and Leute for bulk material (J. Solid State Chem., 43 (1982) 339). Very different nature of the growth habit was observed on the Si(111). High population of planer defects observed in the thin film was regarded as the result of Ga vacancy ordering in the crystal structure of Ga@sub 2@Se@sub 3@. We claim that the vacancies play an important role in determining the thin film structure in addition to lattice and symmetry matching conditions in the heteroepitaxy.

SS-TuP13 Surface Morphology of Ge(111) and Ge(001) Etched by keV Xe Ions*, **J.C. Kim**, D.G. Cahill, R.S. Averback,* University of Illinois, Urbana-Champaign

In situ scanning tunneling microscopy (STM) was used to study the surface morphology and defects created by keV Xe@super +@ ion etching of Ge(111) and Ge(001). Starting surfaces were prepared by etching single crystal Ge wafers at ~ 510 @super o@C by 5 keV Xe@super +@ ions with ion flux of 2.7 x 10@super 13@ ions cm@super -2@s@super -1@ and fluence of 5 x 10@super 16@ ions cm@super -2@; the samples were subsequently cooled and etched at lower temperatures with various ion fluences and ion energies, and imaged at room temperature. Ge(111) and Ge(001) surfaces remain crystalline after being etched at T @>=@ 295 @super o@C. Crater-like surface features, which were not observed on the starting surfaces and will be called pits, were observed on both Ge(111) and Ge(001) surfaces etched at 295 @super o@C and 325 @super o@C. These pits are ~ 200 Å in diameter and are surrounded by closely spaced steps. Pits were observed on the Ge surfaces etched by Xe@super +@ ions with energies as low as 650 eV. Etching of a Ge(111) buffer layer, which was grown at ~ 365 @super o@C with the thickness of 1000 Å in an in situ

MBE chamber, at 295 @super o@ was performed to examine the interaction of 5 keV Xe@super +@ ions with the surface prepared without etching at high temperature and revealed no pits. These results that pits were observed following 650 eV Xe@super +@ ion etching and not observed following etching of an MBE buffer layer suggest that these large surface features are not the result of the individual surface cascades as has been observed for 20 keV Ga ions. The pits initially grow in size and number and eventually disappear after the samples were etched for approximately one hour, leading to different surface roughening morphologies at 295 @super o@C and 325 @super o@C. Rutherford backscattering spectroscopy (RBS) data show that Xe atoms are implanted below the starting surface, subsequent ion etching at lower temperatures causes a broadening of Xe peak in RBS spectra. Our data suggest that interaction of bulk defects, e.g. Xe bubbles or vacancy clusters, with surface can have a strong influence on the evolution of surface morphology during ion etching at keV energies.

SS-TuP14 Surface Core Level Shift on GaN(0001) Surface*, **Y. Yang**, S.H. Xu, H. Cruguel, G.J. Lapeyre,* Montana State University*; H.J. Ho,* TopoMetrix Co.

Synchrotron radiation photoelectron spectroscopy (SRPES) has been employed to investigate the electronic structure of clean wurzite GaN(0001) surface. The Ga 3d, N 1s and valence band emissions are measured by recording the energy distribution curves (EDC). A surface-shifted core level component is observed in the Ga 3d emission. It is located at 0.6 eV higher binding energy than the bulk component. The surface component is sensitive to atomic H adsorption. Experiment with deposition of ultra-thin Mg layer strongly support that it is attributed to the first layer Ga atoms. On the same sample, the surface core level shift of N 1s is identified at 1.0 eV lower binding energy side of the bulk component. The origin of the observed surface core level shifts will be discussed. Atomic-force-microscopy (AFM) image with line profiles are also acquired to determine the surface morphology.

SS-TuP15 Raman-scattering Study of In(As,Sb)/InSb Superlattices*, B. Marcos, R. Cuscó,* Institut Jaume Almera (CSIC), Spain*; R.A. Stradling,* Imperial College, U.K.*; **L. Artús**,* Institut Jaume Almera (CSIC), Spain

InAs@sub 1-x@Sb@sub x@ alloys display the smallest bandgap in the III-V group for x=0.6. By growing In(As,Sb)/InAs superlattices even smaller effective bandgaps can be obtained, making these layer structures very interesting for applications to mid- and far-infrared semiconductor lasers and light-emitting diodes operating at wavelengths from 4 to beyond 10 µm. In a previous paper@footnote 1@ we reported a Raman-scattering study of the optical phonon modes of InAsSb/InAs strained-layer superlattices(SSL) for different Sb compositions, but to our knowledge no study has been reported so far on the phonons of the other end system SSLs, namely the InAsSb/InSb SSLs. In the present work we report Raman measurements on InAsSb/InSb SSLs for several As concentrations below 20%. The InAsSb alloy displays a two-mode behaviour,@footnote 2@ and consequently the InSb-like and InAs-like LO modes of the alloy are expected. In fact, despite the low As concentration of the alloy, in the (Z|XY|-Z) Raman spectra we could observe not only the InSb-like LO mode of the alloy but also the InAs-like LO mode. The strain-induced relative shift of this peak is well accounted for by elastic strain calculations. In the (Z|XX|-Z) configuration an additional peak is observed below the InSb-like LO mode of the alloy that can be tentatively assigned to interface modes. @FootnoteText@ @footnote 1@ L. Artús, R. A. Stradling, Y. B. Li, S. J. Webb, W. T. Yuen, S. J. Chung, and R. Cuscó, Phys. Rev. B 54, 16 373 (1996). @footnote 2@ Y. B. Li, S. S. Dosanjh, I. T. Ferguson, A. G. Norman, A. G. de Oliveira, R. A. Stradling, and R. Zallen, Semicond. Sci. Technol. 7, 567 (1992).

SS-TuP16 The Adsorption and Thermal Decomposition of Monomethylamine Adsorbed on Si(100)*, **A.J. Dennis**, C.P.A. Mulcahy, S.M. Casey,* University of Nevada, Reno

Monomethylamine (MMA) adsorption on the Si(100)-(2x1) surface has been studied using Auger electron spectroscopy (AES), low-energy electron diffraction and temperature-programmed reaction spectroscopy (TPRS). It is shown that at room temperature MMA chemisorbs dissociatively on this surface. TPRS data show that the decomposition of the adsorbed MMA proceeds via two different mechanisms. The surface bound adsorbates can decompose via reactions that form gaseous hydrogen and hydrogen cyanide products; however, they may also decompose via a reaction channel producing gaseous ammonia. AES results show that repeated decomposition of MMA on Si(100) leads to the slow deposition of carbon- and nitrogen-based films. Kinetic analysis of the TPRS data will be discussed along with results from ab initio calculations modeling MMA adsorption on nine-atom silicon clusters.

SS-TuP18 The Formation of di-@sigma@ Bond in Chemisorbed Benzene and Chlorobenzene on Si(111)-7x7*, **Y. Cao**, G.Q. Xu,* National University of Singapore, Singapore

The adsorption of aromatics on Si surfaces has attracted great interests recently. In the present study, the adsorption of benzene and chlorobenzene on Si(111)-7x7 has been studied using high resolution electron energy loss spectroscopy (HREELS) and thermal desorption spectroscopy (TDS). Both chemisorbed and physisorbed benzene were observed at an adsorption temperature of 110 K. Chemisorbed benzene desorbs molecularly at 350 and 364 K while physisorbed molecules desorb at 180 K. In the HREELS studies, two separate energy losses at 2920 and 3025 cm@super -1@ were observed for chemisorbed benzene, attributable to the C-H stretching vibrations of sp@super 3@ and sp@super 2@ carbon atoms, respectively. In addition, the formation of Si-C bond is also evidenced at a vibrational frequency of 540 cm@super -1@. Our results clearly demonstrate that benzene is di-@sigma@ bonded to the adjacent adatom and rest-atom on Si(111)-7x7, forming a 1,4-cyclohexadiene-like structure. The adsorption behaviour for chlorobenzene is quite similar to that of benzene. However, due to the substitution effect of the Cl atom on ring of benzene, a regional-selective adduction of 2,5-sites in chlorobenzene on Si(111)-7x7 is observed, resulting the formation of 2,5-chlorocyclohexadiene like adduct.

SS-TuP19 Dissociative Adsorption of Molecular Hydrogen on Si(001): Energy Dependence, Angular Distribution and Reaction Mechanism*, **M. Duerr**, M.B. Raschke, U. Hoefer,* Max Planck Institut fuer Quantenoptik, Germany

The dissociative adsorption of molecular hydrogen on Si(001) surfaces was investigated by means of supersonic molecular beam techniques and optical second harmonic generation (SHG). Sticking on the flat surfaces shows strong activation with beam energy as well as surface temperature.@footnote 1@ Preparing single-domain surfaces by selectively passivating the step sites of vicinal Si(001) surfaces, polar and azimuthal distributions of the sticking coefficient could be measured. The polar distributions are found to be peaked towards the surface normal. However there is a strong azimuthal dependence, the distribution is considerably narrower (cos@super 12@) for incident angles perpendicular than parallel to the dimers (cos@super 3.5@). For multi-domain surfaces, the reduction of the sticking coefficients is more pronounced than it is to be expected by the reduction of normal energy. Therefore the energetic corrugation dominates the adsorption process. Temperature dependence of the sticking coefficient, deviation from normal energy scaling and azimuthal anisotropy result from the covalent bindings on the semiconductor surface, which lead to a strong corrugation of the potential energy surface and the strong influence of lattice vibrations on reaction dynamics. Proposed defect mediated mechanism, leading to an enhancement of sticking under glancing incidence can be excluded. @FootnoteText@ @footnote 1@ M. Duerr, M. B. Raschke, and U. Hoefer, J. Chem. Phys. (submitted).

SS-TuP20 Silicide Island Nucleation Behavior for Co/Si(111) Studied with STM and LEEM*, **T.H. McDaniels**, P.A. Bennett,* Arizona State University

We have measured the coverage and temperature dependence of island nucleation during deposition of Co on Si(111)-7x7 using STM for low temperature and LEEM for high temperature. Below 500C, 3 distinct structures occur: "lowered" regions mostly on the unfaulted half of the 7x7 unit cell, "raised" regions mostly on the faulted half, and flat island structures with a 2x2 pattern of silicon adatoms. Island density vs coverage follows a growth exponent near 1, suggestive of i=0 behavior (stable nucleus contains a single atom), and the temperature dependence is relatively weak. From 600-900C, the islands are atomically flat CoSi2, and they form only at step edges following completion of a 1x1-RC ("ring-clusters") layer. Island density is now much lower and strongly temperature dependent with an activation energy of approximately 2.0eV.

SS-TuP21 Nickel Graphite Intercalation Compound formed by High Temperature Deposition of Ni on SiC*, **K. Robbie**,* Linköping University, Sweden, Canada*; T. Jemander, N. Lin, R. Erlandsson, G.V. Hansson, L.D. Madsen,* Linköping University, Sweden

While studying the growth of sputter-deposited nickel on 6H SiC (0001) substrates, an unexpected islanded structure was formed. Nickel, deposited at room temperature and annealed to 950 C to form Ni@sub 2@Si, is the most common approach for forming ohmic contacts to n-type

SiC. In this study aimed at gaining understanding of the contact formation process, we sputter-deposited Ni layers of varying nominal thickness (sub- to 1000 monolayers) onto hydrogen-etched on-axis SiC substrates at temperatures ranging from ambient to 1000 C and subsequently annealed to 1000 C. In-situ analysis was performed with RHEED, LEED and/or STM. Unlike all previous experience with Ni deposited onto SiC, we observed the formation of islands of two types, one of which had very steep sidewalls (>60 degrees) and an extremely flat top with a peculiar "stitched" surface structure. Microspot AES analysis has shown that the islands are composed of Ni and C, or Ni, Si, and C, and that the carbon is bound graphitically in both types. Investigations with STM, AFM, and AES, and comparison to literature, has led us to believe that a new type of graphite intercalation compound was formed in the flat topped islands with a composition of approximately NiC@sub 12@, and that Ni on the top graphite sheet produced the "stitched" surface structure observed by STM. Previously, only alkali metals and transition metal chlorides have been shown to intercalate into the galleries of graphite, and the reactivity and instability of these compounds has limited their use in spite of their very exciting electronic, magnetic, and other physical properties.

SS-TuP22 Surface Modification in Heteroepitaxy : Laminar, Crystalline Silicon on CaF@sub 2@, ***B.R. Schroeder***, *S. Meng, A. Bostwick,* University of Washington*; E. Rotenberg,* Lawrence Berkeley National Laboratory*; M.A. Olmstead,* University of Washington

CaF@sub 2@/silicon heterostructures are strong candidates for obtaining visible light emission from silicon. However, the heteroepitaxial growth of laminar, crystalline silicon on CaF@sub 2@(111) substrates is hindered by two factors 1) CaF@sub 2@ surface energy is much lower than that of Si and 2) a strong etching reaction between Si and F. We have overcome these difficulties through surface modification 1) use of arsenic as a surfactant 2) electron irradiation to remove surface fluorine. Low energy (40 eV) electron irradiation removes fluorine (amount of F removed scales linearly with the electron dose) but the films become extremely reactive with oxygen and/or water vapor (even under UHV conditions). Arsenic termination stabilizes this surface and serves as a surfactant for the subsequent silicon growth. X-ray photoelectron spectroscopy shows Ca-Si bonds at the interface and As-Si bonds at the surface. The silicon surface has a bulk-like termination, characteristic of Si(111):As, as evidenced by the 1X1 LEED pattern. X-ray photoelectron diffraction shows that the grown silicon layer is crystalline, rotated 180@super o@ with respect to the CaF@sub 2@ substrate (Type B interface), and completely covers the CaF@sub 2@. Supported by DOE grant DE-FG03-97ER45646/A002.

SS-TuP23 X-ray Photoemission and Near Edge Absorption Studies of Rhenium (VII) Sorption onto Fe-bearing Materials*, **P. Liu**, W.W. Lukens, Jr., E.J. Moler, D.K. Shuh,* Lawrence Berkeley National Laboratory

Technetium (@sup 99@Tc) is a radioactive byproduct of nuclear fission, and its concentration may set the regulatory limit for disposal of nuclear wastes. Therefore, the high solubility and mobility of TcO@sub 4@@sup -@ needs to be addressed. A solution is to reduce Tc@sup 7+@ to Tc@sup 4+@, which is much less soluble and mobile. One method is by adsorbing Tc@sup 7+@ onto surfaces of reducing agents. While previous experiments demonstrated that Tc@sup 7+@ ions were sorbed on and reduced by some materials, the products and the mechanism of sorption and reduction are not fully characterized or understood. Rhenium (Re) has similar redox properties as Tc, and can be treated as a surrogate for Tc in selected systems. Since Re is non-radioactive, experiments are more efficiently performed. A class of possible reductants are Fe, Fe oxides, and sulfides. Sorption samples were prepared by immersing powders of Fe metal, FeO, FeS, and FeS@sub 2@, respectively, in 0.010M Re(VII) solution for 24 hours or longer, during which time the powder and the solution were constantly mixed. The reacted powders were extracted after the mixtures were centrifuged and the solutions decanted. The photoemission of Re 4d and 4f core levels, and NEXAFS of Re N@sub III@ experiments were carried out at the Advanced Light Source. The results reveal that the amount of absorbed Re decreases from Fe metal, through FeO, FeS, to FeS@sub 2@; and that different species of Re are sorbed on surfaces of different Fe-bearing materials, with more oxidized species tending to dominate on the less sorbed surfaces. Together with the pH measurements of the residual solutions, the results suggest that the sorption and reduction of Re on the surfaces of Fe-bearing materials are partially controlled by the final pH of the solution-particle mixture.

SS-TuP24 Epitaxial Growth of Thin Ag Films on Al(001) and Al(110) Surfaces@footnote 1@*, N.R. Shivaparan, M.A. Teter, **R.J. Smith**,* Montana State University

We report the results of a characterization of Ag films (0 to 60 Å thick), deposited onto Al(001) and Al(110) surfaces at room temperature, using high energy ion backscattering and channeling, x-ray photoelectron spectroscopy (XPS), and low energy electron diffraction (LEED). For the Al(001) surface, measurements of the backscattered ion yields from Al and Ag atoms show that the Ag atoms occupy fcc lattice sites and shadow Al substrate atoms. However, the ion scattering yields and photopeak intensities do not follow layer-by-layer model growth curves. Together with the evolution of the Ag 3d core level binding energies and the valence band shape as a function of Ag coverage, these results support a model of interface strain relief by means of Ag-Al alloy formation, with the interface ultimately covered by an ordered, epitaxial Ag film. For the Al(110) surface the observations are closer to those expected for layer-by-layer Ag growth, but still show evidence of some Al diffusion into the well-ordered Ag overlayer. @FootnoteText@ @footnote 1@ Work supported by NSF Grant No. DMR-9710092 and by NASA EPSCoR Grant NCCW-0058 .

SS-TuP25 The Reactivity of Short Chain Alcohols on VC (100)*, **R.L. Guenard**[1]*, University of Houston*; S.S. Perry,* University of Houston, US

The reactions of small chain alcohols on the nonpolar (100) surface of single crystal VC have been studied using temperature programmed desorption (TPD). The surface was prepared by argon ion sputtering followed by electron beam heating to 1400K. The sample was sputtered and annealed between coverages, as well, in order to insure the removal of any oxides formed in the reaction with an alcohol. The results of these experiments showed that VC exhibits selective reactivity towards alcohols including, dehydrogenation and alkene formation. In these TPD measurements, methanol adsorbed both molecularly and dissociatively onto VC. The products of temperature induced desorption being H@sub2@ and CH@sub4@. A molecular desorption reaction path was also observed. For ethanol and isopropanol, the resulting products of temperature induced desorption were notably different from that of methanol. A @beta@-hydride elimination mechanism results in the formation of water and an alkene. Ethylene and water are evolved from the surface when dosed with ethanol, while propene and water are the products evolved when isopropanol is dosed. In both cases the alkene product is separated from the surface at a temperature greater than water desorption. This reactivity of short chain alcohols, observed near room temperature on VC (100), illustrates potential pathways of lubricant degradation and highlights the possible need for passivating additives.

SS-TuP26 Extremely Efficient Electron Stimulated Desorption of Hydrogen from GaN(0001)*, **V.J. Bellitto**[2]*,* Georgia State University*; B.D. Thoms,* Georgia State University, US*; D.D. Koleske, A.E. Wickenden, R.L. Henry,* Naval Research Laboratory

To achieve high etch rates and anisotropy during etching of GaN, high temperatures, reactive chemicals, and/or high ion energies are required. The use of electron or photon stimulated processes for etching may be one method to avoid the use of reactive chemicals, damage produced by high ion energies, and materials limitations imposed by high temperatures. Electron stimulated desorption (ESD) of H from GaN(0001) has been observed and characterized using electron energy loss spectroscopy (ELS). Bombardment with 90 eV electrons produces a reversal of H induced changes in the ELS data at 3.5, 6.6, and 11.7 eV. We attribute the electron-stimulated desorption of hydrogen from surface Ga-H to be responsible for these reversals. The reversal of H induced changes to ELS was monitored versus electron exposure to determine the ESD cross section. We measured a cross section for ESD of H of 2 x 10 @super -17@ cm@super 2@ with a reduction of ~3 for the ESD of D to 7 x 10 @super -18@ cm@super 2@. The cross section for the ESD of H from GaN(0001) is 2 to 4 orders of magnitude greater than reported on Si surfaces. On GaN the cross section for ESD of D is ~3 times smaller than for H, while on Si(100) the ESD of D is ~50 times less than for H. Assuming the ESD of H from GaN(0001) occurs through an electronically excited state, as in the Menzel-Gomer-Redhead (MGR) model, the presence of a large cross section and small isotope effect would indicate slow quenching of the excited electronic state. In general, long-lived surface electronic excitations would result in enhanced efficiencies for electron- or photon-stimulated processes. This extremely fast ESD of H also has consequences for electron spectroscopies (LEED & ELS) of H/GaN using similar electron energies and current densities. For example, under the

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

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

conditions used in these experiments (90 eV, 33 µA/cm@super 2@), 34 % of the surface H is removed in the first minute of electron exposure. In essence, the H is removed from GaN(0001) more quickly than many electron spectroscopies can be performed.

Vacuum Metallurgy Division
Room 4C - Session VM-TuP
Poster Session

VM-TuP1 Pattern Writing by Implantation in a Large-scale PSII System with Planar Inductively Coupled Plasma Source*, L. Wu*, *D.M. Manos, T.J. Venhaus,* College of William and Mary

A large-scale PSII system has been built. With chamber 28.5in in diameter and 20in tall, pulses of up to 100KV, and base pressure in the 10@super -8@torr range, it is one of the largest PSII systems. It has been operated with hot filament, hollow cathode and recently with 22.5-inch diameter quartz window for planar RF ICP. This paper compares implantation with these plasma sources, demonstrating the advantages of RFI. It also reports measurements of the plasma density and spatial distribution using Langmuir probe for different RF power, gas pressure and plasma compositions for implanting alloys. Results of implanting alloys including large-area stainless steel cathodes to reduce field emission are reported. Metallic and semiconductor samples have also been implanted through masks with various plasma compositions to produce small geometric patterns of interest for device manufacturing. The samples are characterized by variable-angle spectrometric ellipsometry (VASE), SEM, AES, SIMS, and XPS, and for electrical and mechanical properties. Depth profiles obtained by VASE, SIMS, AES and XPS are compared to Monte-Carlo calculations (Tri-Dyn, Trim, ProfileCode). Measured lateral and depth profiles are compared to the mask features to assess lateral diffusion, pattern transfer fidelity, and wall-effects on the depth profile. The paper also presents the results of MC-hybrid and PIC calculations of the flux and angle of ion trajectories through the boundary layer predicting the uniformity of flux as a function of 3-D location on objects in the expanding sheath and to evaluate the fidelity of pattern transfer as a function of feature size. Sample heating and diffusion effect is included.

VM-TuP2 Growth of SiC Thin Films on Graphite for Oxidation Protective Coating*, J.-H. Boo*, *M.C. Kim, C.H. Heo, S.-B. Lee, S.-J. Park, J.-G. Han,* SungKyunKwan University, Korea

We have deposited thick SiC thin films on graphite substrates in the temperature range of 700 - 850 @super o@C using single molecular precursors by both thermal MOCVD and PEMOCVD methods for oxidation protection wear and tribological coating. Two organosilicon compounds such as diethylmethylsilane (DEMS), (Et)@sub 2@SiH(CH@sub 3@), and hexamethyldisilane (HMDS), (CH@sub 3@)@sub 3@Si-Si(CH@sub 3@)@sub 3@, were utilized as single source precursors, and hydrogen and Ar were used as a bubbler and carrier gas. Highly oriented polycrystalline cubic SiC layer in [110] direction was successfully deposited on graphite at temperature as low as 800 @super o@C with HMDS by PEMOCVD. In the case of thermal MOCVD, on the other hand, only amorphous SiC layers were obtained with either HMDS or DEMS at 850 @super o@C. From this experiment, we confirmed that PEMOCVD was highly effective process in improving the characteristics of the SiC layer properties compared to those grown by thermal MOCVD. The as-grown samples were characterized in situ with OES and RGA and ex situ with XRD, XPS, and SEM. The mechanical and oxidation-resistant properties have been checked. The optimum SiC film was obtained at 850 @super o@C and RF power of 200 W. The maximum deposition rate and microhardness are 2 µmm/h and 4,336 kg/mm@super 2@ Hv, respectively. The hardness was strongly influenced with the stoichiometry of SiC protective layers. Ar-plasma pre-treatment enhanced the hardness and adhesion between SiC layer and graphite substrate due to a nucleation effect.

VM-TuP3 Novel Technique for Low Temperature Chemical Vapor Deposition of Titanium Thin Films on Mild-Steel Surfaces for Corrosion Resistance*, J.H. Hendricks*, *M.I. Aquino, M.R. Zachariah,* National Institute of Standards and Technology

A novel, low temperature technique for growing titanium films on mild-steel substrates has been demonstrated. This method involves the use of a low pressure (600Pa) co-flow diffusion reactor in which sodium vapor and gas-phase titanium tetrachloride react in the presence of a non-reactive gas, Ar. The reaction chemistry is described by the following equation: 4Na(g) +TiCl@sub 4@(g) --@super Ar(g)@-->Ti(s)+ 4NaCl(g). In this reaction, a gas-phase alkali metal (Na) strips multiple halogen atoms (Cl) from a gas-phase metal halide (TiCl@sub 4@). This allows free Ti atoms to attach to a substrate surface placed within the reaction zone, resulting in the growth of a solid metal film. Previously, we have used this technique to grow Ti and TiN thin films on Cu substrates@footnote 1@ at 610°C and TiO@sub 2@ thin films on Si substrates@footnote 2@ at 600°C. This chemistry should be generic for the deposition of a wide class of metallic and ceramic thin films at deposition temperatures which are significantly lower than conventional techniques, and this technique could potentially be used to grow hard and superhard coatings such as CN and BN. Thermodynamics modeling was used to simulate the reactant concentrations and substrate temperatures at which the salt by-product remains in the gas-phase. The modeling predictions were compared to the experimental results and found to be in good agreement. Using the described technique, we have produced Ti thin films on mild-steel substrates with substrate temperatures of 400°C to 800°C. These temperatures are considerably lower than conventional CVD of Ti which involves the thermal decomposition of titanium tetraiodide at 1000°C to 1200°C.@footnote 3@ Lowering the temperature for Ti deposition on mild-steel is of significance since mild-steel undergoes a phase transition at 723°C.@footnote 4@ The corrosion resistance of the titanium coated mild-steel substrates were evaluated to determine the optimum substrate deposition temperature. The quality and composition of the thin films were analyzed by scanning electron microscopy (SEM), energy dispersive x-ray spectrometry (EDS), and x-ray diffraction (XRD). @FootnoteText@ @footnote 1@J. H. Hendricks, M. I. Aquino, J. E. Maslar, and M. R. Zachariah, Chem. Mater. 1998, 10, 2221-2229. @footnote 2@J. H. Hendricks, M. I. Aquino, J. E. Maslar, and M. R. Zachariah, Material Research Society Proceedings, Nov.30-Dec. 4, 1998, Boston, MA. @footnote 3@M. G. Hocking, V. Vasantasree, and P. S. Sidky, Metallic and Ceramic Coatings: Production, High-Temperature Properties and Applications, John Wiley and Sons: New York, 1989, p. 103. @footnote 4@J. M. Camp and C. B. Francis, The Making Shaping and Treating of Steel, United States Steel Company: Pittsburgh, PA, 1951, p. 1203.

VM-TuP5 Friction Evaluation and Development of Vacuum Materials for Tribological System*, M. Tosa*, *A. Kasahara, Y.S. Kim, K. Yoshihara,* National Research Institute for Metals, Japan

Vacuum materials for movement system requires small friction as well as low outgassing. Friction and outgassing strongly depends on the surface conditions and structures of the materials. It is therefore important to evaluate fiction accurately in-situ in a vacuum as controlling such surface layer structures as contaminates layer, adsorbed layer and oxide layer by changing load and vacuum pressure. We have developed a vacuum friction measurement apparatus to evaluate sliding friction under changing the load from 1N to 0.98 mN and under the vacuum pressure from 10@super5@ Pa to 10@super-8@ Pa. Two strain gauges measure the friction force occurred at the loaded pin on the substrate sheet. The measurement was carried out on the sheets for such vacuum materials as type 304 stainless steel, copper, hexagonal boron nitride (h-BN) segregated copper film on the stainless steel, sintered h-BN plate and titanium nitride (TiN) coated stainless steel. All steel sheets are polished mechanically with diamond powder of 0.3µm in grain size. Co-sputtering deposition of h-BN chips and a copper disc target prepared segregated h-BN film. Titanium nitride was coated on the stainless steel with magnetron sputtering deposition. The result of the measurement in decreasing the vacuum pressure shows that the friction coefficient of h-BN surface segregated copper film on steel keeps about 0.1, which is smaller than any other coefficient. The friction coefficient of copper and TiN coated steel decreased gradually but still larger than that of h-BN surface segregated copper film and the friction coefficient of stainless steel increases very much in decreasing the pressure. The result of the measurement in decreasing the load shows that the friction coefficient of h-BN surface segregated copper film on steel keeps smaller than that of copper and steel sheet. Hexagonal boron nitride segregated copper film can be therefore a good candidate material for vacuum tr! ibological system.

Vacuum Technology Division
Room 4C - Session VT-TuP
Poster Session

VT-TuP1 RGA Spectra of Vacuum System Contamination from Typical Cleaning and Handling Sources*, R.S. Goeke,* *J.A. Romero,* Sandia National Laboratories

A library of typical RGA spectra has been generated for commonly used cleaning and handling materials that may lead to contamination in a baked vacuum system. Some of the materials analyzed were: Nitrile gloves, Brulin & Citrodet aqueous based cleaners, Fluoroware, Scotchbrite pads. Spectra were generated using a UHV desorption system with a Quadrupole Gas Analyzer. The purpose of the analysis was to generate a finger print library of possible contamination sources, which could be used to identify contamination in a production system. @FootnoteText@ 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.

VT-TuP2 Application of Porcelain Enamel as a UHV Compatible Electrical Insulator*, M.D. Mapes,* Brookhaven National Laboratory, usa*; H.C. Hseuh, C. Biscardi,* Brookhaven National Laboratory

Many accelerator vacuum system components require electrical insulation internal to the vacuum system. Some accelerator components at Brookhaven National Laboratory are installed in UHV vacuum systems which require the insulation to have excellent vacuum characteristics, be radiation resitant and be able to withstand high temperatures when used on baked systems. Porcelain enamel satisfies all these requirements. This paper describes the process and application of coating metal parts with porcelain enamel to provide electrical insulation. The mechanical and vacuum testing of Marman flanges coated with porcelain and using metal Helicoflex seals to form a zero length electrical break are detailed. The use of porcelain enameled parts is attractive since it is fast, inexpensive and enviromentaly safe and most of all satisfies stringent vacuum system requirements.

VT-TuP3 High Resolution Quadrupole Mass Spectrometer for Light Masses*, A. Hofmänner, N. Müller,* ***H. Eppler,*** Balzers Instruments, Principality of Liechtenstein

Nuclear fusion experiments are performed with gas mixtures containing several components of low mass number (H2, D2, T2, 3He, 4He etc.). Quadrupole mass spectrometers with unit resolution can not separate these gases because of spectral overlaps even if spectrum- deconvolution algorithms are used. So high resolution mass spectrometry is required to separate the components with identical nominal mass numbers. For high resolution measurements in the low mass range a radiofrequeny-generator was developed that operates in the second Mathieu stability region. It drives a 16 mm rod diameter, 300 mm long mass filter at a frequency of 2.05 MHz and covers the mass range from 0.4 to 16.4 m/e. A cross- beam ion source with magnets produces ions with very good definition of ionization volume and energy. The deflection of the ions by 90Â° onto an off-axis SEM acts as an energy filter and so improves the resolution of the system. For example resolution of >400 at m/e= 4 is obtained with selectable resolution from 0.008 to 0.050 m/e at 10% peak height. The good stability of the mass scale allows for long term measurements without readjustment.

VT-TuP4 The Measurement of Multi-Layer Insulation (MLI) Outgassing and its Impact on Effective Cryostat Pumping*, R.J. Todd,* *D. Weiss, D.J. Pate,* Brookhaven National Laboratory*; R. Davis,* Brookhaven National Laboratory, U.S.

The Relativistic Heavy Ion Collider (RHIC) is a superconducting particle collider that operates at cryogenic temperatures. The magnets used to bend and focus the beam are housed in twelve, 480 meter long, common cryostats. Outgassing rates of the MLI (multi-layer insulation) used in the cryostats were measured. Both the double aluminized mylar and polyester spacer material were tested for outgassing spectra and total quantity outgassed. To achieve a satisfactory base pressure in the cryostat, pumpdown estimates were made using the outgassing data. The number and size of pumps were varied to compare the effect on base pressure and water vapor loading of the pumps. Actual pumpdown curves were measured and compared with estimates. The effects of water vapor loading were also studied.

VT-TuP5 New-type Leak Detector utilizing Oxygen-Ion Conductor (I) --Principle and Fundamental Performances--*, K. Tatenuma,* *K. Uchida, K. Uta, T. Noguchi,* KAKEN Co., Japan*; H. Saeki,* Japan Synchrotron Radiation Research Institute, Japan*; A. Ando,* Himeji Institute of Technology, Japan*; T. Momose,* Miyagi National College of Technology, Japan

We developed a new-type leak-detector [LeakD] with an extraordinary wide pressure range by electrochemical measurement of a partial oxygen pressure utilizing the character and performance of oxygen-ion conducting ceramics, e.g. Yttria Stabilized Zirconia (YSZ). Tests using a vacuum apparatus composed of LeakD, a residual gas analyzer (RGA), a capacitance manometer, a Penning gauge, and a turbomolecular pump, confirmed that the responces of LeakD follows Nernst's law; e.m.f.=RT/nF[ln(P(O@sub 2@)ref/P(O@sub 2@)vac)], where e.m.f.: electromotive force (V), R: gas constant (8.314 J/molxK), T: temperature of probe (K), n: charge number of ionization (4: 2O@super 2-@), F: Faraday constant (9.65x10@super 4@ C/mol), P(O@sub 2@)ref and P(O@sub 2@)vac are oxygen partial pressures at a standard gas and a vacuum, respectively. An oxygen partial pressure in a vacuum is decided from e.m.f. LeakD is simple and small, which composed of YSZ ceramics tube (od.10 mm x id.7 mm x 90 mm (long), sealed at one ended) with porous platinum electrodes on inner and outer surfaces, a heater inserted into the YSZ tube to gain a high oxygen-ion conducting rate, a thermocouple, and two electric wires to measure the e.m.f. between two electrodes. To look for a leak point using LeakD, a gas excluded oxygen, e.g. nitrogen and so on, is blown to a point. LeakD is basically a general oxygen sensor using an oxygen-ion conductor. LeakD can detect a partial oxygen pressure by a function in the ranges from 10@super +2@ to 10@super -20@ atm or less; especially it has detectable leak rate both larger and smaller than He leak rate of RGA.

VT-TuP6 A Unique Cryogenic Pumping System for Space Simulation Chambers*, A.D. Ketsdever,* Air Force Research Laboratory*; F.M. Lutfy, E.P. Muntz,* University of Southern California

To investigate the behavior of spacecraft interactions with the space environment and their own ambient atmosphere (caused by material outgassing or propulsive maneuvering), extremely low chamber background pressures and low backscattering rates from chamber walls are required. For meaningful spacecraft-thruster interaction studies, large pumping rates are also required to maintain background pressures at acceptable levels with high propellant flow rates. For the pumping rates required by some applications, cryogenic pumping appears to be the only adequate choice. In order to have a manageable chamber size, a unique geometrical configuration for the cryogenic pumping system was developed. The pumping system consists of outer liquid nitrogen panels which reduces the heat transfer from the outer chamber walls (300 K) to the inner gaseous helium panels (20 K). The inner cryogenic arrays consist of many radial fins which serve several purposes. First, the fin arrangement increases the available pumping surface area by an order of magnitude over a simple cylindrical geometry. Second, there are gaps between the radial fins which allow heavy ions and radiant heat to impact the graphite covered liquid nitrogen panels. In this way, sputtering from energetic ions is reduced and the liquid nitrogen panels remove most of the heat generated by the thruster. Finally, the fins reduce the solid angle for backscattering from non-condensing chamber surfaces to a particular area of interest. With this configuration, a total chamber pumping scheme has been adopted which uses all of the interior chamber surfaces to condense gases thus reducing backscattered molecules as much as possible.

VT-TuP7 Investigation for Pumping Speed and Foreline Performance of a Turbo Booster Pump*, R.-Y. Jou,* Precision Instrument Development Center,Taiwan, ROC, Taiwan, ROC

A compound or hybrid turbo pump constructed by both of turbo blade and drag pumping elements is usually designed to get the best attributes of both types of pump at the same time. However, the complexities in rotor geometry incur problems for specific applications. A rotor configuration design for the new turbo booster pump which is combined a TMP section with a spiral groove rotor by a specially designed connecting blade and is successfully predicted by both of CFD and DSMC simulation methodologies has been conducted. The predicted and testing results show that this pump is effective to operate in an inlet pressure range from 10-7Torr to around 10Torr with a maximum pumping speed appropriately 1000L/s in free molecular regime. Modern semiconductor processes require a large gas throughput and an ultrahigh vacuum (UHV) pump to create an ultraclean process environment. And to choice a proper foreline pump with effective foreline capabilities to reduce contamination to process chambers is an important consideration issue for pump designs and applications. Therefore, it is imperative to investigate the foreline performance of this pump to optimize its function. In this article, a testing system designed to measure the pumping speeds and the foreline capabilities of this pump is constructed. A conductance valve is attached between the turbo booster pump and the foreline pumps to study the optimum foreline speed for this new pump. By controlling valve conductance between HV pump and foreline pump, and by measuring the variations of pressures and throughput at inlet and outlet, the influences of foreline's speed upon the total performance of turbo booster pump are explored. Besides, to reduce cost of the mechanical booster pump and inherently danger of contamination from it, the substitution possibility using this new pump is also discussed.

VT-TuP8 True and Measured Outgassing Rates of a Vacuum Chamber of a Reversibly Adsorbed Phase*, **K. Akaishi,*** National Institute for Fusion Science, Japan*; M. Nakasuga,* Kyoto University, Japan*; Y. Funato,* Suzuka National College of Technology, Japan

We reported before that the outgassing rates measured in a 304 stainless steel chamber were dependent on pumping speed. So a pump down model based on the Temkin adsorption isotherm was constructed to explain theoretically the dependence of the measured outgassing rate on pumping speed. From the model an outgassing equation was derived, which describes the change of coverage of adsorbed molecules at the wall surface of the chamber with time. Two terms, true and measured outgassing rates of the vacuum chamber, appear in the equation, and it is shown that the true outgassing rate is proportional to the measred outgassing rate and the proportional constant reveals a reduction coefficient for the pumping speed of a vacuum pump. In this paper the magnitudes of the measured outgassing rates as a solution of the outgassing equation are estimated numerically as a function of pumping speed and compared to the measured outgassing data in experiment. A good agreement between theory and experiment for the measured outgassing rates is found.

VT-TuP9 A Vacuum Gauge System with a Self-compensator for Photoelectrons Produced in the SPring-8 Storage Ring*, **H. Saeki,*** Japan Synchrotron Radiation Research Institute, Japan*; T. Momose,* Miyagi National College of Technology, Japan*; H. Yonehara,* Japan Synchrotron Radiation Research Institute, Japan

Some of the Bayard-Alpert gauges mounted on crotch chambers in the SPring-8 storage ring have indicated negative pressures at stored electron beam currents more than 5 mA. Simple measurements determined that negative and lower pressure indications of the vacuum gauges were caused by an influx of photoelectrons to the collectors. Therefore, to measure pressure more accurately in such a hot-vacuum environment, we proposed a vacuum gauge system with a self-compensator for photoelectrons from the environment. The gauge has a correcting electrode which only detects photoelectron current from the environment and obtains the actual pressure by compensating the current detected in the primary collector of the gauge. The estimated actual pressure of the gauge system with a self-compensator is adequate, compared with the apparent pressure detected with Extractor gauges. To make sure of the estimation, the new gauge system will be evaluated with an experimental vacuum chamber which makes such a hot-vacuum environment using an electron gun.

VT-TuP11 Study of Microgeometry of Activated Coals and Non-evaporable Getters*, S.B. Nesterov, Yu.K. Vassiliev,* Moscow Power Engineering Institute, Russia*; **G.L. Saksaganski,*** The Efremov Research Institute of Electrophysica Apparatus, Russia

Determination of the pumping speed is of crucial importance by design of the surface action pumps. Pumping speed depends on the sticking coefficient value. Dependence of the integral sticking coefficient for the whole cryopanel on the local sticking coefficient in the concrete point is being determined in this paper. Real surface of the sorbent is not flat. So a molecule of the pumped gas can be reflected from this surface several times. The real surface of different sorbents - activated coals and non-evaporable getters is analysed by scanning tunnel microscope. To calculate dependence of the cryopanel integral sticking coefficient on the local sticking coefficient on the sorbent surface the test particle Monte-Carlo method is used considering the real surface of a sorbent. Integral coefficient values obtained during the experiment allow one to compute the local coefficient value for the concrete sorbent type. Obtained results for various types of sorbents may be useful for engineers constructors of surface action pumps.

VT-TuP12 RHIC Turbomolecular Pumping System*, **D. Weiss**, R.C. Lee, D.J. Pate, L.A. Smart, D. Zigrosser,* Brookhaven National Laboratory

The Relativistic Heavy Ion Collider (RHIC) Project at Brookhaven National Laboratory (BNL), is a 3.8 km circumference collider commissioned earlier this year. The superconducting magnets used to steer and focus the ion beams, operate at 4.2K, and are contained in 28 cryostats of various sizes. A network of turbomolecular pumping stations (TMPS) is employed to maintain the rough vacuum in the magnet cryostats prior to cooldown of the machine, and to pump helium, which may be present in the cryostats due to leaks in the internal cryogenic distribution system. The design and operation of the TMPS and TMPS network is presented, with particular focus on the integration of off-the-shelf components with the BNL custom designed station logic controller (SLC). Additionally, the performance of the TMPS during the commissioning phase of RHIC is described.

VT-TuP13 Photon Stimulated Desorption Measurements of Copper Beam Chambers for the KEKB Collider@Footnote 1@*, **C.L. Foerster**, C. Lanni,* Brookhaven National Laboratory*; K. Kanazawa,* KEK, Japan*; K. Shimotsuma,* KSA Inc.

KEKB is an asymmetrical collider constructed for the High Energy Accelerator Research Organization(KEK) in Ibaraki, Japan. The new collider utilizes two UHV ring chambers, one for a 3.5 GeV positron beam and the other for an 8 GeV electron beam, to study B-mesons. Two Samples, each one (1) meter long, of KEKB beam chambers were studied on newly constructed beamline U9a at the National Synchrotron Light Source (NSLS). Copper was chosen by KEK for the chamber construction material as it withstands high peak heat loads and also serves as a radiation shield. The samples have a circular cross section of 94mm inner diameter. After cleaning, flanges were electron-beam welded to the ends of the samples, and then the assembly was shipped to the NSLS, for installation in the PSD set up. Once sucessfully leak tested, the sample was installed in U9a, exposed to more than 10@super 23@ photons direct from the source at a critical energy of 595 eV, striking the sample at an incident angle of 100mrad. The major PSD yields for hydrogen, carbon monoxide, carbon dioxide, methane, and water vapor are reported as a funtion of accumulated photon flux and sample preparation. The results are compared with other PSD measurements on NSLS beamlines U9a, U10b, X28a, and those of other laboratories published for copper. @FootnoteText@ @Footnote 1@ Work performed under auspices of the U.S. Department of Energy, under contract DE-AC02-76CH00016.

Applied Surface Science Division
Room 6A - Session AS-WeM
Gaede-Langmuir Award Address and Quantitative Surface Analysis

Moderator: P.M.A. Sherwood, Kansas State University

8:20am **AS-WeM1 Monte Carlo Simulations for Tilted Electron Multipliers@footnote 1@**, ***Y.S. Choi**, S.G. Yu, J.M. Kim,* Samsung Advanced Institute of Technology, Korea

Microchannel electron multipliers are simulated using the Monte Carlo method. Gains of secondary electrons are calculated for different structures of the electron multiplier. For a tilted cylindrical channel of the electron multiplier the gain has a maximum at a tilt angle. The maximum gain is about a thousand times larger than that of the not-tilted channel. An explanation is suggested for the improvement of gain in the tilted channel. @FootnoteText@ @footnote 1@This work was supported by the Korean Ministry of Science and Technology through the Creative Research Initiative program.

8:40am **AS-WeM2 Gaede-Langmuir Award Address: Early Development of Auger and ESCA Instrumention**, ***P.W. Palmberg**,* Physical Electronics **INVITED**

The role of the author in the early development of practical Auger and ESCA instrumentation is reviewed. The significance of these early 1970's developments to the surface science community and industrial users is discussed. The authors contributions to both instrument and application development are outlined.

9:40am **AS-WeM5 Consistent, Combined Quantitative AES and XPS Digital Data Bases - Convergence of Theory and Experiment**, ***M.P. Seah**, I.S. Gilmore, S.J. Spencer,* National Physical Laboratory, United Kingdom

AES and XPS have more aspects in common than they have in distinction. Therefore, tests of aspects for one spectroscopy, applicable to the other, should be validated for both. Digital databases for elemental spectra for both AES and XPS have thus been measured using an electron spectrometer that has fully calibrated intensity and energy axes. This provides true spectra to give absolute Auger electron yields and relative photoelectron yields. The AES database is measured for both 5 and 10 keV electron beam energies, whereas the XPS database is measured for both Al and Mg unmonochromated X-rays at the magic angle. The combination of these databases allows a refinement of the theories to obtain an overall convergence between theory and experiment. Improvements have been obtained by identifying three classes of parameter to consider: (i) parameters for both AES and XPS, such as electron transport, the methodology of evaluation of peak areas and the spectrometer response function, (ii) parameters for AES only, such as the electron ionisation cross section, backscattering and specific electron backgrounds and (iii) parameters for XPS only, such as the photon-ionisation cross section. Using this approach, improvements to the theories of all three classes of parameter and their method of use have been established. The formalism for quantitative analysis in AES and XPS, using relative sensitivity factors, has been revised to develop an accurate matrix-less formalism that is very simple for use by the analyst. This formalism has the same accuracy as the full matrix formalism but its simplicity permits ready extension to systems beyond binary. Details of these and recent advances, particularly with improvements in the background subtraction for the peak area measurement, lead to excellent convergence between theory and the data. This will be discussed, together with outstanding issues for general quantitative analysis with AES and XPS.

10:00am **AS-WeM6 Relationships between Parameters Describing Inelastic Electron Scattering in Solids**, *A. Jablonski,* Polish Academy of Sciences*; **C.J. Powell**,* National Institute of Standards and Technology

The terms inelastic mean free path (IMFP), effective attenuation length (EAL), and mean escape depth (MED) are frequently used to specify the surface sensitivity of AES and XPS and also for quantitative applications. These terms are different conceptually because of the effects of elastic-electron scattering, and generally have different numerical values. In addition, EAL and MED values depend on the instrumental configuration. We apply an analytical formalism developed from a solution of the kinetic Boltzmann equation within the transport approximation@footnote 1@ to demonstrate the relationships between the IMFP, EAL, and MED for selected elemental solids and for common measurement conditions. It is shown that EAL and MED values can be derived from an analytical representation of the emission depth distribution function and values of the IMFP and the transport mean free path.@footnote 2@ Examples are given to show the magnitude of elastic-scattering effects on MED values for angle-resolved XPS and AES. If XPS or AES data are acquired for emission angles between zero and 60°, the ratio of the MED to that found with elastic scattering neglected is approximately constant (to within 10 %), and this ratio can be used to determine an average value for the EAL. This EAL value can then be used to establish the depth scale in the data analysis. For emission angles greater than 60°, conventional data analysis (in which elastic-scattering effects are neglected) becomes unreliable. Finally, we show ratios of the EAL to the IMFP for XPS from the Au 4s subshell with Mg K@alpha@ x rays as a function of emission angle and depth; this ratio has a weak dependence on emission angle from zero to 40° but a more pronounced dependence for larger emission angles. @FootnoteText@ @footnote 1@I. S. Tilinin, A. Jablonski, J. Zemek and S. Hucek, J. Electron Spectrosc. 87, 127 (1997). @footnote 2@A. Jablonski and C. J. Powell, J. Electron Spectrosc. (in press).

10:20am **AS-WeM7 Straightforward Methods for Accurate Estimation of Attenuation Length and Similar Quantities in XPS and AES**, ***P.J. Cumpson**,* National Physical Laboratory, UK*; M.P. Seah, I.S. Gilmore,* National Physical Laboratory, UK, United Kingdom

The surface-sensitivity of X-ray Photoelectron Spectroscopy (XPS) and Auger Electron Spectroscopy (AES) is due to strong inelastic scattering of electrons. Elastic scattering also takes place, and modifies@footnote 1@ the absolute intensities, the sensitivity factors, the intensities from layers, and (in the case of XPS) the asymmetry parameter @beta@, all of which feed-in to quantitative analysis of spectra. The modification is a multiplicative factor of between 3% and 30% depending on the kinetic energy and material. The behaviour of the asymmetry parameter is particularly important for those using monochromated XPS instruments. Elastic scattering affects these quantities in a straightforward way. This leads to some simple recommendations on analysis geometry, and estimation of Attenuation Lengths to optimise the accuracy of quantifications without increasing complexity. One can measure surface composition and layer thicknesses to known, acceptable accuracy,@footnote 2@ provided one can estimate the Attenuation Length of signal electrons in the sample being analysed. In particular, Attenuation Lengths for organic materials are important in defining polymer, lubricant or contamination surface layers by Angle-Resolved XPS. We therefore pay particular attention to how to estimate Attenuation Length values for an arbitrary organic material. These estimates are in excellent agreement with Monte Carlo calculations. @FootnoteText@ @footnote 1@ A Jablonski, Surf. Sci. 364 (1996) 380. @footnote 2@ P J Cumpson and M P Seah, Surf. Interface Anal. 25 (1997) 430.

10:40am **AS-WeM8 Quantitative Auger Spectroscopy: Applications to Process Development and Qualification of Tungsten Silicide Films**, ***C.T. Dziobkowski**, S.C. Ramac,* IBM Corp., E. Fishkill*; E.D. Adams,* IBM Corp., Burlington

Tungsten silicide films are widely used in gate conductors for DRAM gate structures for complementary metal-oxide-silicon (CMOS) integrated circuits. Careful characterization of these films with Rutherford backscattering spectrometry (RBS) and Auger electron spectroscopy (AES), the two most commonly used techniques, helps define and control a practical tungsten silicide process. The correct choice of analytical parameters is essential in obtaining accurate and reproducible compositional analysis. The enhanced depth resolution of Auger spectroscopy is especially critical in viewing the region of the interface between the tungsten silicide and polysilicon. Currently, an intrinsic polysilicon cap is used between the doped polysilicon and the CVD deposited tungsten silicide to prevent an unwanted secondary reaction between phosphorus and tungsten hexafluoride which leads to a tungsten enriched interface. This enriched tungsten interface can result in abnormal oxidation, stress and loss of adhesion between the intrinsic polysilicon and tungsten silicide. AES and RBS analytical techniques have been applied to examining the control of this interface to allow extension of CVD tungsten silicide to the thinner gate polysilicon needed for advanced technologies. Examples will be given of the effects of varied gate cap thickness of both amorphous and intrinsic polycrystalline silicon on the tungsten silicide / polysilicon interface using these analytical techniques. The interface composition is known to have a profound effect on the performance of these devices.

11:00am **AS-WeM9 Naphthalocyanine Molecules onto Si(111)7x7 and Si(100)2x1: Modes of Adsorption and Effects of Oxygen Doping Investigated with XPS***, L. Ottaviano,* INFM, Italy*; **L. Lozzi**, A. Montefusco, S. Santucci,* University of L'Aquila and INFM, Italy

We have deposited in ultra high vacuum various thickness of metal free naphthalocyanine (H@sub 2@NPc) onto Si(111)7x7 and Si(100)2x1 and studied in situ the interfaces by means of standard monochromatized X-ray Photoelectron Spectroscopy.@footnote 1@,@footnote 2@ By comparing the core level N1s and C1s spectra obtained for the pure molecule with those typical of the interface at submonolayer and intermediate level of deposition we derived information on the ways of adsorption of the isolated molecules onto the substrates used. In particular NPc adsorbs planarly to the Si(111)7x7 substrate showing strong chemisorption effects involving all the atoms of the molecule. On the other hand, the chemisorption involves only two C atoms when using the Si(100)2x1 substrate. In this case the NPc molecules are likely to be adsorbed in a out of planar mode. In a dedicated series of experiments, the interfaces have been doped with oxygen. An integer ratio of the estimated oxygen atoms per Naphthalocyanine (NPc) molecule in the quantitative XPS elemental analysis of the spectra gives evidence for a preferential adsorption of oxygen in molecular form onto NPc. A careful analysis of the spectra indicates that oxygen mainly interacts with the inner porphyrin structure of the molecule. @FootnoteText@ @footnote 1@ L. Ottaviano, L. Lozzi, and S. Santucci, Surf. Sci. (in press). @footnote 2@ L. Ottaviano, L. Lozzi, A. Montefusco, and S. Santucci, Surf. Sci. (submitted).

11:20am **AS-WeM10 Technique for Production of Calibrated Metal Hydride Films***, **R.A. Langley**, J.F. Browning, S.D. Balsley, J.C. Banks, B.L. Doyle, W.R. Wampler,* Sandia National Laboratories

A technique has been developed for producing calibrated metal hydride films for use in the measurement of high-energy (5-15 MeV) particle reaction cross sections for hydrogen and helium isotopes on hydrogen isotopes. Absolute concentrations of various hydrogen isotopes in the film is expected to be determined to better than ± 2% leading to the capacity of accurately measuring various reaction cross sections. Hydrogen isotope concentrations from near 100% to 5% can be made accurately and reproducibly. This is accomplished with the use of high accuracy pressure measurements coupled with high accuracy mass spectrometric measurements of each constituent partial pressure of the gas mixture during loading of the metal occluder films. Various techniques are used to verify the amount of metal present as well as the amount of hydrogen isotopes: high energy ion scattering analysis, PV measurements before, during and after loading, and thermal desorption/mass spectrometry measurements. The most appropriate metal to use for the occluder film appears to be titanium but other occluder metals are also being considered. Calibrated gas ratio samples, previously prepared, are used for the loading gas. Deviations from this calibrated gas ratio are measured using mass spectrometry during and after the loading process. These techniques will be discussed and results presented.

11:40am **AS-WeM11 The Role of SIMS for Interface Control in the MBE Growth of InGaSb/InAS Strained Layer Superlattices***, **J.S. Solomon**, M.L. Seaford, D.H. Tomich, K.G. Eyink,* Air Force Research Laboratory

Secondary ion mass spectrometry (SIMS) was used to evaluate beam flux control used for the molecular beam epitaxial (MBE) growth of an indium gallium antimonide/indium arsenide (InGaSb/InAs) strained layer superlattice. Two methods of control were compared: (1) a computer controlled mechanical shutter and (2) a computer controlled system consisting of both a mechanical shutter and a servo operated valve. The issue is the unintentional incorporation of arsenic in the InGaSb layer due to inadequacies of beam flux control mechanisms, such as shutters, to completely shield sources that are part of a cyclic growth process. Test structures of GaAs and GaSb were used in the study with the former used to evaluated antimony control and the latter used to evaluate arsenic control. SIMS results showed arsenic levels as high as 2-4% in GaSb layers when only a mechanical shutter was used. Neither arsenic nor antimony were detected in their respective test structures when growth was controlled with the combination of mechanical shutter and valve. SIMS results correlated with arsenic and antimony levels determined by high resolution x-ray diffraction (HRXRD) analysis of the same test structures. Finally, HRXRD showed improved interface integrity in the SLS structures grown using the combination of mechanical shutter and vale to control arsenic and antimony beam fluxes.

Biomaterial Interfaces Group
Room 613/614 - Session BI-WeM

Cell Solid-Surface Interactions

Moderator: W. Knoll, Max Planck Institute for Polymer Research, Germany

8:20am **BI-WeM1 Fabrication of Biologically Active Interfaces upon Self-Organization of Amphiphilic Polymers***, **T. Nishikawa**, J. Nishida, K. Nishikawa, R. Ookura, S.-I. Nishimura, S. Wada, T. Karino, H. Okubo, M. Matsushita, S. Todo, M. Shimomura,* Hokkaido University, Japan

Fabrication of cell culture substrates possessing micro surface morphology is one of the current topics in biomaterial research. Recently we found that two dimensional honeycomb structures can be fabricated by casting dilute solutions of amphiphilic compounds on solid supports in a humid atmosphere. The structural feature of the honeycomb films is a two dimensional single layer of hexagonally arrayed holes, whose diameter is ranging from 1 µm to 10 µm. We suggest that the honeycomb films work as artificial basal films - biologically active interfaces between cells and solid supports. The porous structure will enable the adhered cells to reach and interact with the surface of solid support as well as the exposed surface of the cast films. The pore size, porosity, and thickness of the films can be major factors which control the cell behavior on the culture substrates. In this sense cell behavior on porous surfaces can be influenced by the surface morphology as well as the chemical properties of the polymers constituting the films. In this report we describe the fabrication of the honeycomb films and the cell culturing on the films from the view point of factors affecting the cell adhesion in detail. Honeycomb films with various pore size and film thickness were fabricated by casting dilute solution of amphiphilic copolymers on water surfaces. The films were transferred onto cell adhesive supports (slide glass) or non-adhesive supports (polyhydroxyethylmethacrylate coated glass plate). Bovine aorta endothelial cells or hepatocytes were cultured on the honeycomb films. The thicknesses of the films were varied with the water temperature of the subphase (at 6°C 0.2 µm in thickness and 4 µm in hole diameter and at 20°C 1.5 µm in thickness and 4 µm of hole diameter). The cell adhesion to the honeycomb films was considerably influenced by the film thickness, which determines the distance between the adhered cells and the solid supports.

8:40am **BI-WeM2 Reactions of Biological Cells to Nanostructures***, **A.S.G. Curtis**, C.D.W. Wilkinson,* University of Glasgow, Scotland

The reactions of biological cells to nanostructured polymer and silica surfaces will be described. The surfaces have been prepared in a variety of materials using E-beam methods, colloidal resists and replication by embossing. The reactios include changes in adhesion and cytoskeletal organisation. The effects of topography in the ranges 20-100nm greatest plan dimension, 50-200nm repeat and 10-100nm height will be described. The degree to which the cells conform to these surfaces will be reported with details of the closeness of approach of the cells to the surfaces. The question of whether the reactions are to topography, chemistry or surface disorder at boundaries will be discussed.

9:00am **BI-WeM3 Engineering Cell Surface Chemistry***, **C.R. Bertozzi**,* University of California, Berkeley **INVITED**

Many important biological processes are initiated by cell surface molecules, such as cell-cell adhesion and communication during development, virus-host cell binding, tumor cell metastasis and immunological recognition. Consequently, the ability to chemically control the display of epitopes on cell surfaces would enable a myriad of possibilities for studying cell-cell interactions and for engineering cells with novel properties. This presentation will focus on work in my laboratory that aims to apply the principles of organic chemistry to orchestrating cell surface chemistry. We have harnessed the cell's metabolic machinery to remodel cell surfaces with reactive organic functional groups. The foundation of our approach is the unnatural substrate tolerance of several enzymes involved in oligosaccharide biosynthesis, which permits the conversion of unnatural monosaccharide precursors into cell surface-associated oligosaccharides. We have exploited these pathways as vehicles for the delivery of uniquely reactive electrophilic functional groups, such as ketones and azides, to cell surfaces. For example, we demonstrated that an unnatural analog of N-acetylmannosamine bearing a ketone group, N-levulinoylmannosamine (ManLev), is metabolized by human cells to N-levulinoyl sialosides on the cell surface, resulting in the cell surface display of ketone groups. The cell surface can then be selectively reacted with rationally-designed organic structures bearing a complementary nucleophile such as an aminooxy group which reacts to form a stable covalent adduct. The ability to engineer chemical reactivity into endogenous cell surface molecules suggests many potential applications including the engineered adhesion of cells to materials and artificial surfaces. @FootnoteText@ @footnote 1@ Mahal, L. K.; Yarema, K. J.; Bertozzi, C. R. Engineering Chemical Reactivity on Cell Surfaces Through Oligosaccharide Biosynthesis. Science 1997, 276, 1125-1128. @footnote 2@ Mahal, L. K.; Bertozzi, C. R. Engineered Cell Surfaces: Fertile Ground for Molecular Landscaping. Chemistry & Biology 1997, 4, 415-422. @footnote 3@ Lemieux, G. A. ; Bertozzi, C. R. Chemoselective Ligation Reactions with Proteins, Oligosaccharides and Cells. Trends Biotech. 1998, 16, 506-513. @footnote 4@Yarema, K. J.; Mahal, L. K.; Bruehl, R.; Rodriguez, E. C.; Bertozzi, C. R. Metabolic Delivery of Ketone Groups to Sialic Acid Residues. Application to Cell Surface Glycoform Engineering. J. Biol. Chem. 1998, 273, 31168-31179. @footnote 5@ Lemieux, G. A.; Yarema, K. J.; Jacobs, C. L.; Bertozzi, C. R. Exploiting Differences in Sialoside Expression for Selective Targeting of MRI Contrast Reagents. J. Am. Chem. Soc. 1999, 121,4278-4279.

9:40am **BI-WeM5 Biocompatibility of Cardiac Cells on Silane-Modified Surfaces***, **J.J. Hickman**, M.S. Ravenscroft, H. Canavan,* The George Washington University*; V. Krauthamer,* Food and Drug Administration

We are investigating the interaction of cardiac cells with select silane-modified surfaces in a defined culture system. Our goal is to examine cell reaction in vitro to the types of modified surfaces that may be useful as implant coatings with an assay that we could relate to organ function. The SAM-modified glass coverslips were analyzed using X-ray Photoelectron Spectroscopy (XPS). The morphology was determined by image analysis and the excitability of the cultured cardiac cells was examined electrophysiologically by Calcium imaging both at rest and while being stimulated. Stimulation experiments electrically pace the cells at select time intervals and monitor the resulting changes in intracellular [Ca]. We observed a significant difference in excitation-induced Ca changes on the different silanated surfaces without corresponding differences in cell morphology. This result implies a change in cardiac Ca channel function on SAMs with different functional groups that would not be detected by morphological analysis alone.

10:00am **BI-WeM6 Biomaterials That Talk***, **P.S. Stayton**, T.C. McDevitt, K.E. Nelson, C.M. Giachelli,* University of Washington*; R.B. Vernon, H. Sage,* Hope Heart Institute*; D.G. Castner,* University of Washington

We are working to develop a variety of biomaterials that are designed to communicate with biomolecules, cells, and tissues. This goal requires complementary surface assembly techniques, engineering of biomolecules designed for surface applications, and detailed characterization of the biomolecules at surfaces. In this talk, I will present joint protein engineering and microfabrication approaches to constructing coatings that control cell phenotype in confined dimensions on device surfaces. These coatings are designed to interact with specific receptors to control cell motility, proliferation, and protect against apoptosis.

10:20am **BI-WeM7 Biofunctionalization of Surfaces with Peptide Amphiphiles***, **M. Tirrell**,* University of Minnesota, U.S. **INVITED**

Peptides carry enormous capacity and versatility for participating in specific ligand-receptor binding interactions. As small fragments of proteins, they offer the possibility of delivering a selected activity in constructing a biofunctionalized surface or interface, absent other, undesired activities present in the full protein molecule (e.g., immunogenicity). We have been exploring the self-assembly and cell recognition properties of peptide fragments (thus far derived from extracellular matrix fragments) that we have lipidated synthetically by attaching a phospholipid-mimic, double-chain, hydrocarbon tail. Lipidation confers interesting amphiphilic and self-organization properties on the molecules and enables the stable deposition of layers of peptide amphiphiles on surfaces. Specifically, we have been using peptide amphiphiles to functionalize surfaces with peptide fragments derived from collagen and fibronectin. Deposition of these molecules by Langmuir-Blodgett methods gives a very high degree of control over the density and orientation of the surface molecules. This in turn enables us explore the effects on cell response of peptide density and molecular architecture variations with a great degree of precision. The principal results so far, which seem to have some generality for different kinds of peptides, are that there is an optimum peptide density for each kind of peptide fragment, and that the architecture of peptide presentation is a very sensitive controller of bioactivity. Examples will be given of these effects.

11:00am **BI-WeM9 Plasma Copolymer Surfaces for Cell Culture***, **R.D. Short**,* University of Sheffield, UK

The plasma copolymerisation of a functionalised monomer with a hydrocarbon diluent comonomer can be used to fabricate surfaces of controlled chemistry. By employing low plasma power, fragmentation can be kept to a minimum and the functional group preserved from the functionalised monomer to the plasma copolymer deposit. This has been demonstrated for carboxyls, carbonyls, alcohols and amines. Changing the ratio of functionalised monomer to hydrocarbon monomer allows films of varying functional group concentration (functional groups per 100 carbons) to be prepared. Substratum surface chemistry is known to play a critical role in the attachment, spreading and proliferation and differentiation of cells in tissue culture. The culturing of different cell types - keratinocytes (primary), endothelial cells (cell line) and osteoblasts (primary and cell line) - on plasma copolymer films containing carboxyl, carbonyl and alcohol functionalities has been investigated. Cell response has been explored with functional group concentration. Optimum attachment, spreading and proliferation were obtained on surfaces containing carboxyl groups - these surfaces contained 3-5 carboxyl groups per 100 carbons. Actin-staining by direct immunofluorescence was used to visualise changes in osteoblast cytoskeleton with substratum chemistry. It was observed that as the substratum carboxyl concentration increased cell spreading was notably enhanced. As few as 5 carboxyls per 100 carbons were sufficient to support good cell attachment and a well-defined polygonal cell morphology on an essentially hydrophobic surface.

11:20am **BI-WeM10 Mechanical Properties of a Bone Marrow Cell-Knit Composite for Tissue Engineering: Evolution under Mechanical Load***, **B. Müller**, G. Ettel, D. Siragusano, T. Brandsberg, F. Brandsberg, M. Petitmermet, A. Bruinink, J. Mayer, E. Wintermantel,* ETH Zürich, Switzerland

Knitted textiles provide a 3D scaffold for optimal spatial and nutritional conditions in engineering biological tissue in vitro. The vital-avital composite formed by the textile fabric and the ingrown cells can be stimulated by mechanical load. Introduced by cyclic stretching it affects the proliferation and differentiation of bone cells as indicated by specific protein synthesis and cell mass increase. As an additional parameter, the evolution of the mechanical properties of the vital-avital composite is in situ measured by a piezoelectric force sensor. The system for the stimulation of in vitro cell cultures is calibrated by the use of a coil spring minimizing frictional losses. Reference measurements are performed using multifilament PET-knits as untreated ones and others saturated with serum proteins. After autoclaving and under constant load, both types of knits show an exponential run-in behavior with a time constant of about 2h. In the frequency range investigated (0.1 to 3.0Hz) the amplitude raise lies between 10 and 15%. Long-term experiments (5 days) with cyclic mobile and immobile phases of 3 and 6 hours, respectively exhibit a linear decrease of 5% in amplitude for the protein saturated knits, however. Finally, the preliminary experiments using primary adult rat bone marrow cells demonstrate that the stiffness of the vital-avital composite increases by a power law as a result of mechanical stimulation (Stretching is as low as 2%). Therefore, the successive force measurements reflect the physiological mechanical state of the cells and, consequently, enable optimizing the properties of the forming tissue. Determinants are the cell density, the stretching, the frequency of mechanical excitation, and the time span for mobile and immobile phases. A mathematical model developed on the basis of nonlinear mesoscopic elasticity theory describes the experimental observations.

11:40am **BI-WeM11 The Effect of Lipopolysaccharide Structure and Composition on Microbial Cell Adhesion***, **S. Kim**, J. Curry,* University of Arizona

Lipopolysaccharide (LPS), the main component of the outer membrane of Gram negative bacteria, consists of a lipid component, termed lipid A, that anchors the LPS in the outer membrane, a sugar core, and a variable O-specific polysaccharide chain. Whenever a bacterium approaches a surface, LPS predominantly mediates the interaction because of its inherent location on the cell surface. Varying size and structure of LPS molecule depending on bacterial strain appears to be an important determinant of the overall charge and hydrophobic character of the cell surface. Furthermore, some workers have shown that change in its chemical composition or pattern lead to a dramatic change in its biological activity. Those facts suggest that studying adhesion as a function of LPS structure and chemical composition may help to better understand the mechanisms of bacterial adhesion. The overall goal of our research is to understand at the molecular scale how the structure and composition of the LPS affects bacterial adhesion and biological activity by direct force measurement using the Surface Forces Apparatus (SFA). Specifically, we will measure the force of interaction and adhesion between two hydrophilic (bare mica) and hydrophobic (surfactant coated) surfaces in the presence of LPS molecules at different environmental conditions (i.e. temperature, pH, ionic strength). Samples used in this study will be several rough mutant LPS (R-form) molecules of which structures are well characterized. Along with the knowledge of their structure and chemical composition, the complete force profile will allow us to better predict adhesive properties of several different types of bacteria. This work will be very meaningful for research in many areas where microbial adhesion is important, for instance, biofilm formation and microbial transport in porous media.

Electronic Materials and Processing Division
Room 6C - Session EM+NS-WeM

Nano-characterization of Molecules, Materials, and Devices

Moderator: R.S. Goldman, University of Michigan

8:20am **EM+NS-WeM1 Homoepitaxy on AlSb(001): Novel Reconstructions and Their Implications for Nucleation and Growth*, W. Barvosa-Carter,*** HRL Laboratories*; A.S. Bracker, J.C. Culbertson, B.V. Shanabrook, B.R. Bennett, L.J. Whitman,* Naval Research Laboratory*; N. Modine,* Sandia National Laboratories*; H. Kim, E. Kaxiras,* Harvard University

Strained-layer heterostructures involving the 6.1 Å family of III-V semiconductors (InAs, GaSb, and AlSb) are being investigated for use in a growing number of high-frequency and infrared devices. The structure of the interfaces in these heterostructures can be critical to device performance, and device optimization will ultimately require precise and reproducible control over surface morphology during growth. To accomplish this level of morphological control, models are being developed which relate process parameters to surface roughness. These models require a detailed understanding of the relevant surface reconstructions and the mechanisms by which epitaxy proceeds. Using MBE, RHEED, and STM (performed at NRL), combined with first-principles theoretical calculations, we have discovered a novel (4x3) reconstruction on the nominally "(1x3)" AlSb(001) growth surface. This new reconstruction is different than those previously proposed for this surface and, surprisingly, includes mixed III-V dimers in the top layer of the reconstruction. The presence of surface Al atoms close to their natural lattice sites leads to nucleation and growth mechanisms that are fundamentally different than for III-As systems. We have also studied AlSb homoepitaxy as a function of coverage. The relationship between the observed reconstructions, island structure, island distributions, and possible growth modes will be discussed.

8:40am **EM+NS-WeM2 A New Point Projection Microscope for the Holographic Imaging of Single Macromolecules*, A. Eisele,*** *B. Völkel, A. Glenz, B. Jäger, A. Gölzhäuser, M. Grunze,* Universität Heidelberg, Germany

In Low Energy Electron Point Source microscopy the spatial coherence of electrons from point sources can be utilized to image single molecules. A molecular object is positioned ~100 nm in front of the source and interference patterns between the part of the electron's wave function that scatters at the object and the part that passes by unscattered are recorded.@footnote 1@ Structural information on the molecule can then be obtained by numerical reconstruction of the hologram.@footnote 2,3@ We have built a new microscope for the recording of holograms at high magnification (@>=@10@super 6@) and under the minimization of critical disturbances like vibrations and alternating magnetic fields. In the presented instrument projection microscopy can be interleaved with in-situ preparation of the source via field emission / field ion microscopy. The microscope has been tested by the imaging of single DNA molecules that were deposited on thin structured siliconmembranes. Numerical reconstructions of the obtained holograms show corrugated strands with a diameter of ~2 nm. @FootnoteText@ @footnote 1@ H.-W. Fink, W. Stocker, and H. Schmid, Phys. Rev. Lett. 65, 1204 (1990) @footnote 2@ H. J. Kreuzer, K. Nakumura, A. Wiezbicki, H.-W. Fink, and H. Schmid, Ultramicroscopy 45, 381 (1992) @footnote 3@ A. Gölzhäuser, B. Völkel, B. Jäger, M. Zharnikov, H.J. Kreuzer, M. Grunze, J. Vac. Sci. Technol. A16(5), 3025 (1998)

9:00am **EM+NS-WeM3 Single Molecule Vibrational Spectroscopy with a Variable Temperature STM*, L.J. Lauhon,*** *W. Ho,* Cornell University **INVITED**

The ultimate sensitivity for vibrational spectroscopy is the detection of a single bond. The vibrational spectrum of a single molecular adsorbate carries information about the effects of the local environment on chemical bonding. Such effects are the basis of important processes such as catalysis. Single bond sensitivity was recently demonstrated by using a scanning tunneling microscope to perform inelastic electron tunneling spectroscopy (STM-IETS) on a single acetylene molecule.@footnote 1@ We have extended this technique to other molecules at temperatures from 8 K to 60 K in an effort to both better understand and widen the applicability of STM-IETS. Two 'tunneling-active' vibrational modes have been identified for CO adsorbed on Cu(001) and Cu(110). The effects of monatomic steps and coadsorbed potassium on the vibrational spectra, including peak shifting and quenching, were found to be local in nature. The increase in the vibrational peak width with temperature was measured up to 40 K, beyond which thermal diffusion prevented STM-IETS spectra from being recorded. STM-IETS was also performed on pyridine and benzene adsorbed on Cu(001). Though these molecules differ only in the substitution of a nitrogen atom for one C-H group, their bonding geometries and vibrational spectra are very different. Achieving the spatial limit of nanotechnology depends on the ability to perform chemistry on the atomic scale. To this end, tunneling electrons were used to dissociate individual pyridine and benzene molecules. The adsorbtion geometries of the reaction products differ from the parent molecules and lead to changes in the vibrational spectra which provide insights into the identities of the reaction products and the tunneling mechanism. The extension of STM-IETS to new functional groups, including larger molecules, will also be discussed. @FootnoteText@ @footnote 1@ B. S. Stipe, M. A. Rezaei, and W. Ho, Science Vol. 280, p. 1732 (1998).

9:40am **EM+NS-WeM5 Characterization of Electronic Materials and Devices by Scanning Probe Microscopies*, C.C. Williams,*** *V. Zavyalov, L. Klein,* University of Utah*; J. Kim,* Korea Advanced Institute of Science and Technology **INVITED**

Several studies of the electrostatic properties of oxides and silicon devices have been performed by the Scanning Capacitance Microscope (SCM) and the Electrostatic Force Microscope (EFM). The SCM provides a method for measuring topographical and electrical roughness of thin oxides, surface charge and local carrier and dopant density in semiconductors. On thin oxides, the SCM reveals a nanometer scale variation in the "electrical thickness" of the oxide. The thickness variations seen by SCM have been compared with topographical (AFM) and surface potential measurements by EFM in UHV. Surface potential variations of order 5 mV are observed on the same spatial scale as the thickness variations seen by the SCM. Calculations show that the measured surface potential variations correspond to less than one electron per tip area (30 nm radius). Single MOSFET devices have been imaged in cross-section under active electrical bias by SCM. The images provide a measure of the distribution of the carriers in a device under bias. Finally, a new technique will be described for detecting the transfer of a single electron between a SPM tip and surface.

10:20am **EM+NS-WeM7 Mapping Composition and Electrostatic Potential in Devices*, A. Ourmazd,*** *A. Orchowski, W.-D. Rau, P. Schwander,* IHP, Germany **INVITED**

An electronic device is, in essence, a microscopically varying electrostatic potential surface, which steers the charge carriers between the device's terminals. Until recently, there were no means for directly measuring the electrostatic potential distribution in the bulk of devices. It is now possible to map the electrostatic potential in two dimensions by electron holography. Maps of deep submicron transistors have been obtained with nanometer spatial resolution and 0.1V sensitivity. The electrostatic potential surface can be tailored by changes in composition and/or doping. It is often important to separate the two effects. Electron holography alone, however, cannot distinguish between them; they both change the electrostatic potential. QUANTITEM, on the other hand, is sensitive to compositional changes only. Efforts are under way to combine the results from electron holography and QUANTITEM, in order to separate the effects of composition and doping, with first encouraging results.

11:00am **EM+NS-WeM9 Failure Analysis of Sub 1/4-Micron Contacts by Means of TEM-EELS*, F. Yano,*** *Y. Nakamura, T. Aoyama, Y. Mitsui,* Hitachi Ltd., Japan

Although TEM-EELS (Transmission Electron Microscope-Electron Energy Loss Spectroscopy) has practically been used for elemental analysis for nanometer area, its full potential, we believe, is achieved when it is used for chemical analysis just like ESCA. This paper uncovers our experience of thermally stable contact development, in which our advanced TEM-EELS@footnote 1@ has revealed reactions in the contact during thermal process, which have detrimentally increased its resistivity.@footnote 2,3@ The contact holes are filled with sputtered Ti, which is annealed to form TiSi@sub 2@, CVD-TiN and CVD-W. Alathough the contact resistivity was low enough just after contact processes, it became higher after thermal process. The resistivity was varied 10@super 2@ to 10@super 6@ @ohm@ depending on the process conditions. Chemical analysis of loss energies showed that Si substrate in the contact is fully covered with SiO@sub 2@ in the fatal worst case. Even somewhat better cases, TiSi@sub 2@ formation was partial and still SiO@sub 2@ was formed. In other cases, TiO@sub x@ was also observed. These oxidized layers clearly increased resistivity. However, the mechanism of oxidation was unclear, especially the origin of the oxygen was, because neither oxygen nor water was applied. To clarify the mechanism, we made a model, in which residual TiCl@sub x@ on CVD-TiN forms titanium acid gel (TiO@sub x@(H@sub 2@O)@sub n@) which works as a water reservoir. During thermal process, the water in the gel is released, which goes through TiN grain and finally oxidizes silicon at the interface of TiN and Si substrate. To prove this model, the relation between the amount of residual Cl and the contact resistivity was measured. The results supported the model above, i.e., the more Cl observed, the higher the resistivity is. Based on this mechanism, all cases of high resistivity failures in the thermally stable contact were explained. Chemical analysis by TEM-EELS will be a key technique for failure analysis of 1/4-micron devices and after. @FootnoteText@ @footnote 1@ T. Sekiguchi, et al., Jpn. J. Appl. Phys., vol. 37 (1998) L694. @footnote 2@ Y. Mitsui, et al., Ext. Abst. IEDM (1998) 329.@footnote 3@ Y. Nakamura, et al., Proceedings of Advanced Metallization Conference, Colorado (1998) 661.

11:20am **EM+NS-WeM10 Applications of AFM/SCM in Imaging Implant Structures of Semiconductor Devices*, K.-J. Chao*,** *J.R. Kingsley, R.J. Plano, X. Lu, I.D. Ward,* Charles Evans & Associates

The scanning capacitance microscopy (SCM) has been widely used to investigate the two-dimensional carrier profile of semiconductor devices. In this work, SCM is used to investigate several different semiconductor devices. First, one commercially purchased integrated circuits (IC) device was cross-sectioned and polished for the SCM investigation. Implant structures near the gate were clearly resolved. Second, two semiconductor devices, one was good and the other was failed, were prepared by cross-sectioning and then followed by polishing. Implant profiles of similar structures on both devices were revealed by SCM. As compared with the good device, the thickness of the N-well structure was found to be thinner by about 0.4um for the failed device. Third, a GaAs device with Zn thermally diffused through the Si3N4 mask was studied to determine the lateral diffusion length of Zn. Applications in other cases will be presented at the conference.

11:40am **EM+NS-WeM11 Capacitance Measurements on Gold Nanowires*, A. Wlasenko,*** McGill University, Canada

There are several assumptions made about classical capacitors (C=Q/V): the density of states(DOS) of the plates is infinite, the potential drop occurs entirely across the plates, electrons don't interact, and there is no tunnelling. In mesoscopic capacitors, the voltage drop doesn't occur entirely across the plates, and the finite DOS plays an important role. In the experimental setup presented, the voltage-dependence of C is measured for gold nanowires allowing the DOS to be deduced according to theory [H. Guo et al., APL 74, 2887-2889 (1999)]. A piezotube is used to retract a gold sample in contact with a gold tip to form a nanowire. Along with measurements of C, simultaneous measurements of conductance(G) are made with a current preamplifier to monitor the transmission properties of the contact. Changes in the C of this nanowire are measured by a modified RCA Video Disc sensor: a resonant circuit is connected to a 915 MHz oscillator, and the amplitude of the signal is measured. A change in C leads to a shift in the resonance peak which is detected by the sensor. The sensor is calibrated using a ball bearing and metal plane geometry in comparison with classical calculations. The sensor is sensitive to C changes as low as 10@super -17@ F. When the tip and sample are in contact, the sensor measures a convolution of C and G. Where a variation in C leads to a shift in the resonance peak, a variation in G leads to a change of the FWHM. Measurements on either side of the resonance peak can be made in order to seperate C and G.

Magnetic Interfaces and Nanostructures Technical Group Room 618/619 - Session MI+EM-WeM

Spin-Dependent Tunneling and Transport

Moderator: K. Bussmann, Naval Research Laboratory

8:20am **MI+EM-WeM1 Models of Spin-dependent Tunneling*, S. Zhang*,** University of Missouri, Rolla **INVITED**

There are a number of theoretical models of spin-dependent tunneling. Some are based on toy models and others are built on electronic structures of ideal tunnel junctions obtained from ab-initio methods. The question is whether these models are relevant to the experimental realization of the magnetotransport of magnetic tunnel junctions. We analyze these model predictions by taking into account non-ideal nature of the magnetic tunnel junctions studied to date. It is shown that most of the theoretical conclusions are not reliable in interpreting experimental data. There are at least three intrinsic mechanisms on the voltage dependence of magnetoresistance: the effect of electronic structure, inelastic tunnel channels, and spin-dependence of electric field penetrations. The last effect comes from spin-polarized electron screening. When a voltage is applied across a magnetic tunnel junction, charges and spins are accumulated at the interfaces. The conduction electrons tend to screen these charges and spins via Coulomb and exchange interactions; this leads to a spin-dependent voltage absorption by the electrodes. We calculate the voltage dependence of magnetoresistance by including this field penetration effect. When one considers magnetic tunnel junctions beyond simple trilayer structures, e.g., double barrier junctions, a number of additional complications arise. Among them, the energy and spin relaxation of tunnel electrons becomes important. We examine these processes in detail, and present the I-V characteristics and junction magnetoresistance for both two-terminal and three-terminal geometries.

9:00am **MI+EM-WeM3 High Performance Demonstration of Magnetic Tunnel Junction Random Access Memory**, W.J. Gallagher*,** *S.L. Brown, Y. Lu, E.J. O'Sullivan, P.L. Trouilloud, D.A. Abraham, J. Bucchignano, R.H. Koch, Y.H. Lee, R. Robbertazzi, M. Rooks, J. Yoon, R.A. Wanner, S.S.P. Parkin, D. Pearson, K.P. Roche, M.G. Samant, P.M. Rice, A. Lee, R.E. Scheuerlein,* IBM **INVITED**

We describe a magnetic tunnel junction (MTJ) RAM demonstration involving the integration of 0.25 µm CMOS technology with a special research-scale magnetic tunnel junction "back end." The magnetic back end is based upon state of the art mutilayer magnetic growth technology available on a research scale. For the demonstration, the wafers were cut into one-inch squares for depositions of bottom-pinned exchange biased magnetic tunnel junctions. The samples were then processed through four additional lithographic levels to complete the circuits. Special care was required to achieve fine lithography on the one-inch pieces aligned to the underlying circuits. Both deep uv stepper lithography and e-beam lithography were utilized. Patterning of the magnetic layers involved physical removal of the magnetic material by means of ion beam milling, an etching process not commonly used in semiconductor technology. Redeposition, which accompanies ion milling and is exacerbated in dense arrays, had to be carefully controlled with combinations of angled mills in order to minimize the occurrence of junction shorts and maximize the yield of working bits. Key performance aspects demonstrated in 1 K bit arrays included reads and writes in less than 10 ns and nonvolatility. These results suggest that MTJ MRAM might simultaneously provide much of the functionality now provided separately by SRAM, DRAM, and NVRAM. . @FootnoteText@ @footnote *@ Work supported in part by DARPA contract MDA972-96-C-0014.

9:40am **MI+EM-WeM5 Pinhole Decoration in Magnetic Tunnel Junctions*, D. Allen*[1]**, *R. Schad, G. Zangari, I. Zana, D. Yang,* University of Alabama; *M.C. Tondra, D. Wang,* Nonvolatile Electronics

Magnetic tunnel junctions are of interest for their possible applications in magnetic sensors and nonvolatile memory devices. The possibility of local shortcuts in the insulating layers of magnetic tunnel junctions, known as pinholes, can cause malfunctions in these devices. The reduction of insulator thicknesses will make this problem more severe. The ability to image pinholes could lead to further development of magnetic tunnel junctions. The imaging of structures that are not directly observable with imaging is traditionally done by decoration. This can be achieved by exploiting the conductivity of the pinholes. We decorated pinholes in a 1.8nm thick Al@sub2@O@sub3@ layer by electrodeposition of copper.

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[1] **Falicov Student Award Finalist**

These copper cauliflower-like structures can be imaged by conventional microscopies. Dielectric breakdown could be a source of pinhole creation. Applying 0.5 V for electrodeposition (as used here) would exceed the breakdown threshold for weak points in the insulator. This would create pinholes at points with insulator thickness less than 0.5 nm. This is an opportunity of the method. Upon application of increasing voltage pulses prior to deposition it will allow discrimination of potential breakdown spots as a function of their thickness. The chemical conditions were tailored to avoid damaging the insulator layer or creating new pinholes. This was verified by studying surface roughness (Atomic Force Microscopy), chemical composition (X-ray Photoelectron Spectroscopy) and layering quality (X-ray Diffraction).

10:00am **MI+EM-WeM6 Novel Hybrid Magnetoelectronic Device for Magnetic Field Sensing**, ***D.M. Schaadt**, E.T. Yu, S. Sankar, A.E. Berkowitz,* University of California, San Diego

Structures in which magnetic and electronic materials are combined offer a variety of possibilities for realization of devices with dramatically improved functionality or performance as compared to conventional devices. We have designed, characterized, and analyzed a novel hybrid magnetoelectronic device: a monolithic field-effect-transistor-amplified magnetic field sensor in which a granular Co-SiO@sub2@ tunnel magnetoresistive (TMR) thin film is incorporated into the gate of a p-channel Si metal-oxide-semiconductor field-effect transistor (MOSFET). In this structure, current flow through the TMR film leads to a buildup of electronic charge within the gate, and consequently to a transistor threshold voltage shift. For a fixed voltage applied across the TMR layer, an external magnetic field changes the TMR film resistance, and consequently the current and charge within the gate. The resulting threshold voltage shift leads to a pronounced response to the external magnetic field in the transistor current-voltage characteristics. The relative current change induced by application of a 6 kOe external magnetic field at room temperature was amplified from 5% for the current through the TMR film to 21% for the transistor subthreshold current. The absolute current response in the saturation regime increased by a factor of about 500 compared to that of the TMR film alone. These results were achieved in a non-optimized device structure; substantially better performance should be achievable with relatively straightforward improvements in device design and processing. A detailed analysis of the operation of this device and of methods for optimization of performance will be presented.

10:20am **MI+EM-WeM7 Andreev and Conduction Electron Spectroscopy of Interfacial Spin Transport**, ***R.A. Buhrman**,* Cornell University **INVITED**

The enhanced interfacial conductance of an N-S contact, due to the Andreev reflection of electrons with energy below the superconducting energy gap, provides a powerful means of measuring interfacial transmission rates, as well as any net spin polarization in the non-superconducting electrode. Thus very small F-S nanocontacts can be used to quantitatively measure the interfacial transmission probability for each spin orientation. This technique can also be extended to the determination of the spin-dependent transmission rates through thin magnetic layers. We have produced F-S and N-F-S nanocontacts lithographically, and have determined the net spin-polarization of the direct current emerging from several bulk ferromagnetic films, and the spin filtering behavior of ultra-thin ferromagnetic layers. Measurements with different N electrodes illustrate the importance of the band structure mismatch in determining the degree of the spin-filtering. The bias dependence of the nanocontact interface resistance in the normal state can also be used to examine the degree to which the interface results in inelastic, spin-flip scattering processes. For certain N electrodes, very strong inelastic scattering is observed at relatively low energies. I will compare these single interface measurements with the current-perpendicular-to-the-plane magnetoresistance results that we have obtained with spin-valve and GMR nanopillar devices less than 100 nm in diameter. The low energy spin filtering measurements will also be compared with higher energy, ~ 1eV, spin filtering measurements that our group has been conducting with an STM-based magnetic microscope.

11:00am **MI+EM-WeM9 Spin-Polarization of La@sub 2/3@Sr@sub 1/3@MnO@sub 3@**, ***D.C. Worledge**, T.H. Geballe,* Stanford University

Spin-polarized tunneling measurements using La@sub 2/3@Sr@sub 1/3@MnO@sub 3@/SrTiO@sub 3@/Al tunnel junctions are reported. The deposition technique and efforts to control the interface quality will be discussed. At sufficiently low temperatures the application of an applied magnetic field splits the peaks in the dI/dV curve, allowing a measurement of the spin polarization to be made.

11:20am **MI+EM-WeM10 Electrical Spin Injection into LED Heterostructures**, ***B.T. Jonker**, B.R. Bennett,* Naval Research Laboratory; *G. Kioseoglou, A. Petrou,* State University of New York, Buffalo

Optical excitation has routinely been used to create spin polarized carrier populations in semiconductor heterostructures. Surprisingly long spin lifetimes and diffusion lengths have been reported in optically pumped GaAs in studies which have addressed both semi-classical@footnote 1@ and quantum coherent regimes.@footnote 2,3@ It is very desirable to electrically inject spin polarized carriers via a ferromagnetic contact to increase the potential for practical applications. This has been an elusive goal, however, and only modest effects (@<=@ 1%) have been obtained.@footnote 4@ In an effort to investigate the efficiency of electrical spin injection into semiconductors, we have fabricated light emitting diode structures with ferromagnetic contacts. The radiative recombination of spin polarized carriers in quantum wells results in the emission of circularly polarized light, with the degree of optical polarization directly proportional to the carrier spin polarization. The samples consist of FM / InAs / AlSb / GaSb / AlSb heterostructures grown by MBE on p-GaAs(001) substrates in which the GaSb quantum well serves as the active region for radiative recombination. Standard optical lithography and chemical etch procedures were used to define mesa structures with transparent surface contacts. Measurements are performed as a function of injection current, magnetic field, and temperature. We compare results from ex situ contacts with those obtained from samples for which the ferromagnetic films are deposited in situ via MBE. @FootnoteText@ @footnote *@ This work was supported by the Office of Naval Research. @footnote 1@ D. Hagele, M. Oestreich, W.W. Ruhle, N. Nestle and K. Eberl, APL 73, 1580 (1998). @footnote 2@ A.P. Heberle, W.W. Ruhle and K. Ploog, PRL 72, 3887 (1994). @footnote 3@ J.M. Kikkawa and D.D. Awschalom, PRL 80, 4313 (1998); Nature 397, 139 (1999). @footnote 4@ Y.Q. Jia, R.C. Shi and S.Y. Chou, IEEE Trans. Magnetics 32, 4707 (1996).

11:40am **MI+EM-WeM11 Electron Spin Interferometry**, ***C.H. Back**, S. Egger,* ETH Zürich, Switzerland; *J. Krewer,* Blaupunkt-Werke GmbH, Germany; *D. Pescia,* ETH Zürich, Switzerland

Quantum interference of electron waves in Fabry-Perot type solid-state resonators has been observed in a number of experiments. The applications of this phenomenon include quantum-well based semiconductor devices,@footnote 1@ accurate mapping of the band structure of solids and surfaces@footnote 2,3,4,5@ and visualizing the spatial dependence of quantum mechanical wave functions by means of Scanning Tunnelling Spectroscopy (STS).@footnote 5@ Here we use quantum interference to switch the spin state of the electrons. The spin quantum resonator consists of a Cu-film of variable thickness sandwiched between vacuum and a magnetic Co-film. Electrons are injected into the resonator from the vacuum side. The Co-film provides a spin dependent reflector. Varying the resonator thickness results in periodic switching of the spin state of the specularly reflected electrons. We apply spin interferometry to study oscillatory interlayer exchange coupling and find a divergence of the coupling period predicted by theory.@footnote 6@ We discuss the implications of spin interferometry as spin polarimeter or spin polarized source and propose that interferometric spin selection should be observable in Spin Polarized STS. @FootnoteText@@footnote 1@Corcoran, E., Diminishing Dimensions, Sci.Am. 263, p.74-83, November Issue, (1990). @footnote 2@Paggel, J.J., Miller, T., Chiang, T.-C., Quasiparticle Lifetime in Macroscopically Uniform Ag/Fe(100) quantum Wells, Phys.Rev.Lett.81, 5632-5635, (1998). @footnote 3@Ortega, J.E., Himpsel, F.J., Mankey G.J., Willis, R.F., Quantum-well states and magnetic coupling between ferromagnets through a noble-metal layer, Phys.Rev.B 47, 1540-1552 (1993). @footnote 4@Kawakami, R.K. et al., Quantum-well states in copper thin films, Nature 398, 132-134 (1999). @footnote 5@Crommie, M.F., Lutz, C.P., Eigler, D.M., Imaging standing waves in a two-dimensional electron gas, Nature 363, 524-527 (1993). @footnote 6@Edwards,D.M., Mathon, J., Oscillations in exchange coupling across a nonmagnetic metallic layer, J.Magn.Magn.Mat. 93, 85-88 (1991).

Manufacturing Science and Technology Group
Room 611 - Session MS-WeM

Metrology I

Moderator: B. Van Eck, Sematech

8:20am **MS-WeM1 Low Open Area Endpoint Detection of Plasma Etching Processes***, **B.E. Goodlin**, H.H. Sawin,* Massachusetts Institute of Technology

Accurate determination of endpoint in plasma etching processes is essential to decrease defects due to both incomplete clearing of the etched material and excessive overetch of the underlying material, leading to a loss of dimension control. This is particularly challenging for low open area etches (<1%), where traditional sensors are at the limits of their sensitivities in determining endpoint. In previous work, we have investigated the use of multivariate analysis to improve the signal to noise of optical emission spectroscopy (OES) data. Improvements of signal to noise of well over 1000% was achieved versus the typical univariate endpoint detection mechanisms employed in industry. Nevertheless, in the lowest open area cases(<1%), difficulty was encountered due to the nonstationary time series behavior of the optical emission signals during main etch. This nonstationary behavior greatly obscured the ability to detect endpoint in these cases. In this work, we have explored several techniques by which to remove time series behavior in optical emission signals. After applying appropriate time series models, the revised data was then analyzed using a multivariate Hotelling's T2 method to see whether endpoint could adequately be detected in low open area etches. The results from historical data are very encouraging and further studies are underway to determine the robustness of this technique.

8:40am **MS-WeM2 Broad Band RF Based Sensing and Control of Reactive Ion Etching***, **C. Garvin**, J.W. Grizzle,* The University of Michigan

This talk will present continued advances in the development of an in-situ RF sensing system for plasma assisted microelectronics processing. RF sensing has long been considered a potentially valuable diagnostic. However, despite much effort, results to date have been limited and mostly qualitative. Our past work has indicated that these limitations are due to inherently poor sensitivity in passive RF sensing. In addition, we have shown significantly better sensitivity to process conditions using a novel multi parameter variation of microwave spectroscopy, referred to as Broad Band RF. On a research reactor (GEC) and for simple chemistries, a non commercially viable version of the broad band probe was shown to be substantially better than standard RF sensing approaches at detecting process setpoints.@footnote 1@ Recently, we have developed a commercially viable non-contacting version of our broad band sensor, and have implemented it on a Lam 9400. The sensor has been used to develop an etch rate model for polysilicon in a Cl2/HBr chemistry.@footnote 2@ In this talk, we will present continued progress towards process control with the broad band sensor. Initial results indicate the broad band sensor is capable of endpointing performance that is at least as good as standard photo diode based OES methods. We will present further advances in a broad band etch rate model. Initial data indicates that an oxide etch rate model is at least as good as the polysilicon etch rate model already presented. Finally, we will investigate physically dominated and chemically dominated etch regimes in more detail. We will present results of initial work in these areas. @FootnoteText@ @footnote 1@ Garvin, C. Grimard, D. S., and Grizzle, J. W. "Advances in Broadband RF Sensing for Real-time Control of Plasma-Based Semiconductor Processing" JVSTA, Jul/Aug 1999 @footnote 2@ Garvin, C. Bilén, S. G. Stutzman, B. S. and Grizzle, J. W. "Implementing Broad Band RF Sensing on a Lam 9400 Reactor", The Electrochemical Society 195@super th@ Meeting, May 2-6 1999

9:00am **MS-WeM3 Diagnostic and Plasma Etch Endpoint Applications using Full Spectrum Optical Emission Spectroscopy***, **H.M. Anderson**,* University of New Mexico*; S. Gunther, W. Branagh, J. Rivers, B. Fry,* CETAC Technologies

The advantages of full spectrum optical emission spectroscopy (OES) over monochromator based systems has been readily demonstrated. Traditionally, monochromator based systems have been used to determine endpoint by monitoring one or two strongly emitting wavelengths. For exposed open areas of <1.0%, a more sensitive approach is required for the next generation of chips. Array detector based systems can provide a wealth of spectral information from a variety of potentially useful gas phase emitting species. In the case of particularly challenging applications such as reverse mask shallow trench isolation (STI) and contact etches, utilization of the full optical emission spectrum has been shown to provide tangible benefits. Production facility results regarding these and other demanding applications will be presented. The talk will largely focus on oxide etching in AMAT MXP and AMAT HDP platforms. Evolving Window Factor Analysis (EWFA) and Multiple Curve Resolution (MCR) are the princpal multivariate techniques used in the analysis. They allow one to dynamically track the principal components of the oxide etch process. EWFA is also shown to useful for automatic fault detection. MCR is used to depict the dynamic rate of formation (or depletion) of the principal chemical species in the plasma during the etch.

9:20am **MS-WeM4 Real Time Control of Plasma Deposited Optical Filters by Multiwavelength Ellipsometry***, **T. Heitz**,* CNRS-Ecole Polytechnique France, FRANCE*; P. Bulkin,* CNRS-Ecole Polytechnique France*; A. Hofrichter,* CNRS-Ecole Polytechnique France, FRANCE*; F. Chataignere, B. Drevillon,* CNRS-Ecole Polytechnique France

Multilayer and gradient coatings allow the integration of advanced functionnalities. But due to their complexity, in-situ probes are necessary to control the process and obtain a good reproducibility. Our optical filters (Fabry-Perot, anti-reflective or heat-reflecting coatings) consist of SiO@sub x@N@sub y@ multilayers and/or graded index profile structures deposited at room temperature in an IDECR reactor on glass, PMMA or polycarbonate. Due to its thickness sensitivity, multiwavelength UV-visible phase-modulated ellipsometry was chosen to monitor the growth process. The control strategy is based on minimising the sum of the distances between the measured point and the theoretical end point of the optical trajectory at 4 wavelengths. This strategy is proved to be very efficient and independent of the deposition rate. As substrates are thick and transparent, the theoretical trajectories have been calculated using the incoherent reflection model which takes into account backreflection. Moreover, to model possible anisotropy effects, optical calculations have been developed based on a non-diagonal dielectric matrix for the susbtrate. In order to build a closed-loop automation system, efficient algorithms have been developed to determine in real time the optical properties and the current deposition rate. Using 4-wavelength optical data, 1 sec step acquisition and appropriated dispersion laws, the refractive index and the current thickness can be calculated which allows to correct in real time the gas flow values. The high quality of the filters deposited using the ellipsometric monitoring system is demonstrated by comparing experimental and theoretical transmission/reflection curves in terms of peak positions and bandwidth.

9:40am **MS-WeM5 Real Time and Run-to-Run Process Control of Plasma Processes Using Internal Machine and External Sensor Data***, **F.H. Bell**, D. Knobloch,* Infineon Technologies AG, Germany*; J. Zimpel, K. Voigtlaender,* Fraunhofer Institute, Germany*; J. Mathuni, P. Hoehmann,* Infineon Technologies AG, Germany

An automatic extraction of key numbers (per wafer) from internal raw machine data and external sensor data has been established for the supervision of plasma equipment and processes in high volume logic and DRAM fabs. The integration of external in-situ sensors in the fab-network of the different sites is realized using the home-built equipment integration software TICS (Tool Integration Concepts and Systems). One main goal of the external sensor integration is to establish plug-and-play modules, i.e. rapid integration of suitable sensors tackling equipment and process faults. Furthermore, analyses of online data over long time periods give information on tool- and chamber- matching, long term stability, trends over cleaning cycles, influence of recipe / product mix, first wafer / conditioning effects and arcing phenomena. Currently in use are electrical and optical sensors, such as optical emission spectroscopy, interferometry, ion flux probe, plasma impedance monitor. etc.. However, the more useful data is collected the more attention has to be paid on intelligent data treatment. A typical example is the need of data reduction in order to extract only process and equipment relevant key numbers. It will be shown that algorithms, such as principal component analyses, are excellent candidates to simplify the use of process control methods in a manufacturing environment. This talk will analyze the different approaches to control equipment and processes and the challenges that are faced by the semiconductor industry as the automation becomes more and more mandatory in the competition of IC-fabrication. Examples of real time control will also be given to demonstrate the benefit of sensors on manufacturing issues.

10:00am **MS-WeM6 Advanced Endpoint Capability in Plasma Processing Equipment Using Interferometer Technique***, **T. Ni**,* Lam Research Corp.

A new interferometer system has been developed at Lam Research Corp.. It provides capability of in-situ etch depth measurement and can be used as an endpoint device when the traditional OES system fails. It consists of a light source and a CCD array spectrometer. A fiber optic cable delivers the light from the lamp to the center of a wafer being processed at normal incident angle. The CCD array spectrometer records the spectrum of the reflected light from the wafer surface. The optical window for light access is engineered to prevent polymer deposition. The analysis of the spectrum yields the thickness information of the films on the wafer. Frequently, the etch depth can be obtained by simply counting the interferometric fringes. With the use of a deep UV light source, an etch depth as shallow as 1000A can be accurately measured. The advantage of the interferometer is demonstrated for applications such as shallow trench isolation (STI) and recess etch. The traditional OES system cannot provide an endpoint signal since there is no stopping layer. Using the interferometer, the etch depth is monitored and etching process can be stopped when the desired depth is reached. In the case of poly gate etch with a very thin (10A-20A) gate oxide underlayer, the interferometer can be used to predict the remaining poly layer thickness so the process can be changed from the main etch process to the overetch process before the oxide layer is exposed. A typical overetch process has greater than 200:1 selectivity to underlayer, while the main etch selectivity typically is much less. Thus, punching-through of the oxide layer is prevented. The details of the interferometer and process results will be presented and discussed.

11:20am **MS-WeM10 Reaction Sensing in Multicomponent CVD Processes using an Acoustic Sensor***, **L. Henn-Lecordier**, G.W. Rubloff, J.N. Kidder, Jr.,* University of Maryland*; C. Gogol, A. Wajid,* Leybold Inficon Inc.

Downstream or in-reactor chemical sensing provides information about the extent of reaction in a chemical vapor deposition process. Prior approaches have employed mass spectrometry or optical techniques. Here we utilize for this purpose an acoustic sensor which measures the sound velocity in bicomponent or multicomponent gas mixtures in the viscous flow regime. This sensor, the recently introduced Leybold Inficon Composer@super TM@, has been employed primarily to measure and confirm bicomponent inlet mixtures from MOCVD bubbler sources for process reproducibility. Here we have explored its use in downstream locations, either after or at the reactor, where the influence of the CVD reaction can be monitored in the form of gas composition changes resulting from reactant depletion and/or product generation. For W CVD processes, the heavy WF@sub 6@ reactant mixed with H@sub 2@ or SiH@sub 4@ provides substantial molecular weight contrast, so that depletion of WF@sub 6@ is readily observed. To achieve sufficiently high pressures (~50-100 torr) for acoustic wave propagation in a viscous medium, sensing is carried out downstream of a mechanical pump. For H@sub 2@/WF@sub 6@ mixtures, depletion levels as small as 1% or less are detectable. This is sufficient for wafer state thickness metrology and monitoring of reactant utilization efficiency, suggesting a promising approach to reaction metrology. However, the corrosive nature of the reactant gasees normally necessitates a N@sub 2@ purge of the pump. With the molecular weight of typical H@sub 2@/WF@sub 6@ mixtures close to that of N@sub 2@, this degrades sensitivity to of order several %. A variety of other implementation issues will be discussed, along with an assessment of a variety of process applications.

11:40am **MS-WeM11 Improvements in Wafer Temperature Measurements***, **A. Cardoso**, A.K. Srivastava,* Eaton SEO

Accurate and repeatable wafer temperature measurement and control is critical in many semiconductor processing applications. Many of these applications are done at moderate pressures (.5 - 2 Torr) where thermal contact resistance between the wafer and a contact temperature probe is high, and could vary wafer-to-wafer. The result is an unpredictable difference between the actual wafer temperature and contact measurement probe due to heat transfer across this interface from exothermic reactions, hot plasma gases, or radiant heating. In some applications, this temperature difference is so great that backside helium cooled electrostatic chucks are used to minimize this effect. In many applications, the use of this type of solution is not practical but accurate and repeatable wafer temperature measurement is still required. A new temperature sensor has been developed that utilizes gas injection through a pinhole in a thermocouple pad that creates a "micro-environment" between the pad and the wafer. This results in reduced thermal contact resistance, and more accurate and repeatable temperature measurement. Temperature data on the operation of this sensor during wafer processing will be presented, showing significant improvement over prior state of the art. Data verifying the robustness of this probe will be shown. Additionally, diffuse reflectance spectroscopy will be used as a non-contact temperature measurement technique to corroborate data from the new gas-cushion thermocouple.

Nanometer-scale Science and Technology Division
Room 612 - Session NS-WeM

Nanopatterning

Moderator: C.R.K. Marrian, Naval Research Laboratory

8:20am **NS-WeM1 "MILLIPEDE" - A Highly Parallel, Very Dense AFM-Based Data Storage System***, **P. Vettiger**, M. Despont, U. Drechsler, U. Dürig, W. Häberle, M.I. Lutwyche, H. Rothuizen, R. Stutz, R. Widmer, G.K. Binnig,* IBM Research Division, Zurich Research Laboratory, Switzerland **INVITED**

We report on an alternative storage approach based on scanning probe techniques having areal density potential far beyond and data rates comparable to today's magnetic-recording techniques.@footnote 1,2@ Ultra-high areal density is achieved by thermomechanical writing/reading in very thin polymer films, and the high data rate by highly parallel operation of very large, 2D cantilever/tip arrays.@footnote 2@ Potential for ultra-high density was demonstrated by 40-nm bit indents and 40-nm bit pitch in 50-nm-thick polymers films (PMMA), resulting in 400 Gbit/sq inch.@footnote 3@ We also demonstrated, for the first time, large area thermal data erasing/rewriting in such polymer films. First functional 32x32 (1024) cantilever array chips were fabricated,@footnote 4@ which are among the densest VLSI-NanoEMS chips. The 32x32 array is fabricated on an 3x3 mm area of a 7x14-mm silicon chip. Four integrated approaching/leveling sensors in the four corners control the simultaneous approach of the entire chip. While the feedback control system keeps the chip leveled and the tips in contact with the media, the media is scanned in the X and Y directions. Writing/reading is controlled by a time-multiplexed row/column addressing scheme. Similar micromaching techniques were used to fabricate a silicon micromagnetic X/Y/Z scanner with integrated Cu coils.@footnote 5@ We present details on the MILLIPEDE storage concept, the thermomechanical write/read/erase processes/results as well as the VLSI-NEMS chip and micromagnetic X/Y/Z scanner fabrication. @FootnoteText@ @footnote 1@ H.J. Mamin et al., IBM J. Res. Develop. 39, 681 (1995). @footnote 2@ P. Vettiger et al., Proc. Int'l Conf. on Micro- and Nanoengineering 98, Leuven, Belgium, Sept. 1998, to appear in J. Microelectron. Eng. @footnote 3@ G. Binnig et al., Appl. Phys. Lett. 74, 1329 (1999). @footnote 4@ M. Despont et al., Technical Digest MEMS'99, p. 564 (IEEE, 1999). @footnote 5@ M. Lutwyche et al., Proc. 194th ECS Mtg., Boston, MA (in press).

9:00am **NS-WeM3 Scanning Probe Lithography of Silicon Nitride Thin Films***, **F.S.-S. Chien**,* National Chiao Tung University, Taiwan*; S.W. Lin,* National Tsing Hua University, Taiwan*; W.-F. Hsieh,* National Chiao Tung University, Taiwan*; Y.-C. Chou, T.-T. Chen,* National Tsing Hua University, Taiwan*; T.S. Chao,* National Nano Device Laboratory, Taiwan*; S. Gwo,* National Tsing Hua University, Taiwan

Silicon nitride has been extensively used as etch stops, diffusion barriers, oxidation masks, and gate dielectric layers in integrated circuit processing. A new method is proposed here to perform local oxidation and negative pattern transfer on silicon nitride thin films. A LPCVD silicon nitride film of 25 Å thickness grown on a p-type silicon wafer is locally oxidized by the probe of an atomic force microscope under positive biases of 5 V to 10 V. In this approach, nanometer-size oxidation patterns can be made on the silicon nitride film. By using the selective HF etching, the oxidized regions on the silicon nitride film can be removed. In a second step, the orientation dependent KOH etching, which has an extremely large selectivity between silicon and silicon nitride, can produce high-aspect-ratio trenched structures (pattern transfer of the original oxide mask) on the (110)-oriented silicon wafer. Such a new method of producing negative-resist pattern tranfer can greatly enhance the capabilities of scanning probe lithography for the future microelecronics and optoelectronics applications on the nanometer scale. @FootnoteText@ F. S.-S. Chien is also with Center for Measurement Standards, Hsinchu, Taiwan.

9:20am **NS-WeM4 Nanolithography and Pattern Transfer of (110)-oriented Silicon Using Scanning Probe Lithography and Anisotropic Wet Etching***, **C.-L. Wu**,* National Tsing Hua University, Taiwan*; S.-S. Chien, W.-F. Hsieh,* National Chiao Tung University, Taiwan*; T.-T. Chen, Y.-C. Chou, S. Gwo,* National Tsing Hua University, Taiwan

Recently, scanning probe lithography has became an emerging technology capable of fabricating sub-micron structures. We have demonstrated that silicon nanostructures (~60 nm lateral dimension) with high aspect ratios and large structural heights (~400 nm) may be fabricated by scanning probe lithography and aqueous KOH orientation-depentent etching on the H-passivated (110)Si wafer. The High spatial resolution of fabricated features is achieved by atomic force microscope based nano-oxidation process in ambient and anisotropic selective wet etching. Combining the large (110)/(111) anisotropic ratio of etch rate and large Si/SiO@sub2@ etch selectivity of aqueous KOH etching at an optimal concentration and a relatively low etching temperature, structural ridges of high-aspect-ratio and excellent parallelism as well as a hexagonal pit structure determined by the terminal etch geometry can be obtained. This method is potentially useful for simple and reliable high-packing-density and high-aspect-ratio micromachining on the nanometer scale.

9:40am **NS-WeM5 Patterning of Silicon Surfaces With a Non-Contact Atomic Force Microscope: Attomol Chemistry and Nanofabrication***, **R. Garcia**, M. Calleja,* Consejo Superior Investigaciones Cientificas, Spain*; H. Rohrer,* Switzerland

Nanometer-size water bridges have been used to confine the anodic oxidation of silicon surfaces with a non-contact atomic force microscope. The formation of a water bridge between two surfaces separated by a gap of a few nanometers is driven by the application of an external electrical field. Once a liquid bridge is formed, its length and neck diameter can be modified by changing the tip-sample separation. The liquid bridge provides the ionic species and the spatial confinement to oxidize Si(100) surfaces.@footnote 1,2@ The very small number of active ionic species within the bridge, a few attomoles, allows a precise control of the lateral and vertical size of the oxide. Above results are applied to develop a highly reproducible method to nanofabricate two types of patterns: (i) arrays of 5000 dots with a periodicity of 40 nm and an average width of 10 nm and (ii) lines 10 micron long and 10 nm wide. @FootnoteText@ @footnote 1@R. Garcia, M. Calleja and F. Perez-Murano, Appl. Phys. Lett. 72, 2295 (1998). @footnote 2@R. Garcia, M. Calleja and H. Rohrer, J. Appl. Phys. (in press).

10:00am **NS-WeM6 Fabrication of Nanoscale Metal Wires on the Si(001) Surface Using Scanning Tunneling Microscopy***, **T. Mitsui**, E. Hill, R. Curtis, E. Ganz,* University of Minnesota

Nanoscale wires are fabricated on the Si(001)-(2x1) surface using an atomic hydrogen resist process.@footnote 1@ The patterning is achieved by removing small areas of the hydrogen passivation layer with a scanning tunneling microscope. Pattern transfer is performed by chemical vapor deposition (CVD) or physical vapor deposition (PVD). CVD provides higher selectivity than PVD. However, Ti selective CVD growth from TiCl@sub 4@ is self limiting by Cl passivation. Growth can be resumed by removing the Cl passivation locally using the STM. Al selective CVD produces 3 nm wires although the wires appear to be granular and sequential growth roughens the pattern. To improve the wire quality, we are now using selective Pd silicide growth by PVD. @FootnoteText@ @footnote 1@T-C. Shen, C. Wang, G. C. Abeln, J. R. Tucker, J. W. Lyding, Ph. Avouris, and R. E. Walkup, Science 268, 1590 (1995).

10:20am **NS-WeM7 Growth and Characterisation of Submicrometer Regular Arrays of Pillars and Helices***, **M. Malac**, R.F. Egerton, M.J. Brett,* University of Alberta, Canada

The fabrication of photonic bandgap structures presents one of the current challenges in microfabrication. Submicron periodic structures with a high aspect ratio are necessary to create a structure with a photonic bandgap in the visible or near infrared region. We have fabricated arrays of pillars and helices with lattice parameter down to 300nm and aspect ratio as high as 25. We utilize oblique-angle deposition onto a rotating substrate (GLAD technique) to grow our films. A square array with lattice parameter between 300 nm and 1 micrometer was patterned onto the substrate prior to film growth. The array was made using electron beam lithography based on PMMA resist followed by lift-off. The array provides preferential sites for shadowed film growth when the film is deposited onto a substrate which is oblique with respect to the arriving species. This method provides a high degree of process control and sufficient number of degrees of freedom to allow for the growth of a wide range of structures. Our microstructures were made of titanium or bismuth, chosen for the large difference in their melting points. All films were deposited onto a room-temperature substrate, implying a low adatom diffusion length for titanium (due to a low ratio of substrate temperature and melting point) but a large adatom diffusion length for bismuth (where bulk diffusion may play a significant role). The titanium pillar structures appear to be uniform along their length, the crystallite size being smaller than the pillar diameter. Regular arrays of titanium helices exhibited bifurcation within each helix, whereas bifurcation was strongly suppressed in both helices and pillars made of bismuth. The delibrate introduction of a defect into the patterned array did not have a radical effect on film growth.

10:40am **NS-WeM8 Plasma Polymerization as a Novel Means of Preparing Concentric-Tubular Composite Microstructures***, **E.R. Fisher**, M.L. Steen, J.R.D. Peers,* Colorado State University

Template synthesis has been shown to be a general method for preparing micro- and nanostructured materials. This method entails synthesizing a desired material in the pores of microporous filtration membranes. Concentric-composite micro- and nanostructures have also been prepared by the template method. Such concentric-tubular structures consist of an outer tubule of one material surrounding inner tubules of different materials. Synthetic methodologies for preparing concentric-tubular micro- and nanostructures include electroless deposition of Au, electropolymerization of metals and semiconductors, carbonization of polymer precursors, chemical-vapor deposition and sol-gel synthesis. Thus, these methodologies are used to prepare composite micro- and nanostructures composed of metals, semiconductors, carbon, polymers and Li@super +@-intercalation materials. We propose an alternative synthetic methodology to preparing concentric-tubular micro- and nanostructures of this type. This method employs plasma polymerization to deposit polymeric conformal coatings on Au micro- and nanotubules synthesized by the template method. There are several experimental advantages to using plasma polymerization. Polymer-formation occurs from almost all volatile organic molecules, even those lacking vinyl and aromatic groups necessary for other polymerization schemes. The chemical composition of the deposited films can be controlled by adjusting plasma parameters, such as applied rf power, monomer flow rate, and pulsed vs. CW conditions. An extensive parameter study of several plasma systems has been examined. We have prepared several Au-insulating and Au-conducting polymer concentric-composite micro- and nanostructures by plasma polymerization. For example, polystyrene-coated Au microstructures are obtained from a pulsed benzene plasma. Results from scanning electron microscopy and electrochemical characterization will be discussed.

11:00am **NS-WeM9 Fabrication of Bismuth Nanowires with a Silver Nanocrystal Shadowmask***, **S. Choi**, K. Wang,* University of California, Los Angeles*; M. Leung, G. Stupian, N. Presser, B. Morgan, R. Robertson, E. King, M. Tueling,* Aerospace Corporation*; S. Chung, J. Heath,* University of California, Los Angeles*; S. Cho, J. Ketterson,* Northwestern University

There has been much interest in arrays of bismuth (Bi) nanowires for both fundamental understanding and device application because of many interesting properties such as long mean free path of the carriers and the small effectiveness and the semimetal-semiconductor transition. In this abstract, we describe a method of using silver (Ag) nanocrystal wires as a shadowmask to produce nanometer-size Bi wire patterns and discuss transport properties of Bi nanowires. In our technique, organically functionalized Ag nanocrystals (2-100nm) can assemble into lamella (wire-like) phases. The width of the wires could be controlled from 20 to 300nm. The wire patterns can be transferred as Langmuir-Scheffer (horizontal lift-off) films to the polymethyl methacrylate (PMMA) coated Bi/CdTe substrates. Bi epilayers were grown by molecular-beam epitaxy (MBE) on CdTe (111) B substrates. X-ray diffraction showed only sharp (00.l) peaks were present, which implied c-axis growth of Bi perpendicular to the substrates. Cleanness of surface of Bi films was also confirmed by the Time-Of-Flight Secondary Ion Mass Spectroscopy (TOFSIMS) using high energy Gallium ions. The wire patterns were transferred to the PMMA films by spatially selective electron beam exposure on the Ag nanocrystal wire shadowmask. 50 nm and 70 nm wide Bi wire patterns were formed by a subsequent anisotropic reactive ion etching (RIE) process. The metal contacts on the Bi nanowires were prepared by in-situ Focused Ion Beam (FIB) deposition for temperature dependent resistance measurement. In zero magnetic field, the temperature dependent resistance measurements on the Bi nanowires with widths of 50 nm and 70 nm showed the resistance increased with decreasing temperature, which was characteristic for semiconductor and insulators.

11:20am **NS-WeM10 Fabrication of Metal Nano-wires using Carbon Nanotube Masks***, **W.S. Yun**,* Seoul National University, Republic of Korea*; K.-H. Park, J.S. Ha, K. Park,* ETRI, Republic of Korea*; J. Kim,* KRISS, Republic of Korea*; S.K. Kim,* Seoul National University, Republic of Korea*; J.-P. Salvetat, L. Forró,* EPFL, Switzerland

Circumventing problems lying in the conventional lithographic techniques, we devised a new method for the fabrication of nanometer scale metal wires using the unique characteristics of carbon nanotubes (CNTs). Since carbon nanotubes could act as masks when CNT-coated thin Au/Ti layer on a SiO@sub 2@ surface was physically etched by low energy argon ion bombardment (ion milling), Au/Ti nano-wires were successfully formed just below the CNTs exactly duplicating their lateral shapes. Cross-sectional analysis by transmission electron microscopy revealed that the edge of the metal wire was very sharply developed indicating great difference in the milling rates between the CNTs and the metal layer as well as the good directionality of the ion milling. We could easily find a few nanometer-wide Au/Ti wires among the wires of various widths. After the formation of nano-wires, the CNTs could be pushed away from the metal nano-wire by atomic force microscopy. The lateral force for the removal of the CNTs is dependent upon the width and shape of the wires. Resistance of the metal nano-wires without the CNTs was also measured through the micro-contacts defined by electron beam lithography. Since this CNT-based lithographic technique is, in principle, applicable to any kinds of materials, it can be very useful in exploring the fields of nano-science and technology, especially when it is combined with the CNT manipulation techniques.

11:40am **NS-WeM11 Strain Effects on the Growth Modes at Stepped Surfaces*, D.Y. Petrovykh*,** *J.-L. Lin, J. Viernow, A. Kirakosian, A. Li, F. Liu, M.G. Lagally, F.J. Himpsel,* University of Wisconsin, Madison

Strain and atomic steps have been used previously to control size, spacing and alignment of self-assembled nanostructures. In this study we utilize high quality Si(111) stepped surfaces as templates for growth of CaF@sub 2@ nanostructures.@footnote 1@ The growth modes in this system in the submonolayer coverage regime are strongly influenced by strain. The step flow mode is expected for deposition rates and substrate temperatures used in our experiments. Instead the growth results in strings of islands attached to step edges. Only for coverage around 0.5 monolayer and above we observe continuous stripes characteristic of the step flow mode. The above two regimes may be beneficial for self-assembly of quantum dot and wire arrays respectively. It has been recently suggested@footnote 2@ that the misfit strain is responsible for the initial roughening of the growth front and formation of islands. Beyond a critical coverage the roughening is suppressed by the interaction between islands on adjacent terraces and continuous stripes become more favorable. A quantitative comparison of experimental results with theory is presented. @FootnoteText@ @footnote 1@ J. Viernow, J.-L. Lin, D.Y. Petrovykh, F.M. Leibsle, F.K. Men, F.J. Himpsel, Appl. Phys. Lett. 72, 948 (1998); J. Viernow, D.Y. Petrovykh, F.K. Men, A. Kirakosian, J.-L. Lin, and F.J. Himpsel, Appl. Phys. Lett. 74, 2125 (1999); D.Y. Petrovykh, J. Viernow, J.-L. Lin, F.M. Leibsle, F.K. Men, A. Kirakosian, F.J. Himpsel, J. Vac. Sci. Technol. A17, July/August (1999). @footnote 2@ Adam Li, Feng Liu, D.Y. Petrovykh, J.-L. Lin, J. Viernow, F.J. Himpsel, M.G. Lagally (to be published).

Plasma Science and Technology Division
Room 609 - Session PS-WeM

Feature Profile Evolution

Moderator: J. Chang, University of California, Los Angeles

8:20am **PS-WeM1 The Ion-Assisted Etching and Profile Development of Silicon in Molecular and Atomic Chlorine*, E.S.G. Shaqfeh,*** Stanford University **INVITED**

An ion beam etching study, designed to characterize the important kinetic and transport processes involved in the ion-assisted etching of silicon in both molecular and atomic chlorine, was performed. Monoenergetic argon ions were directed normal to a silicon wafer that was simultaneously exposed to a neutral molecular and/or atomic chlorine beam. Dissociation of the beam was induced by thermally heating the graphite tip of the effusive source via electron impact. Beam composition was characterized using a quadrupole mass spectrometer. Unpatterned polysilicon wafers were etched to determine the ion-induced etching yields as a function of ion energy, ion to neutral flux ratio, and neutral flux composition. A physically-based kinetic model was developed to represent the yield data, incorporating chlorine adsorption, atomic to molecular chlorine surface recombination, and the ion-induced desorption of adsorbed chlorine and silicon chloride products. Feature etching experiments using patterned silicon wafers were also performed under ion-limited and neutral-limited conditions of varying neutral composition. Resulting profiles were examined for aspect ratio dependent etching effects, where traditional lag was observed for features etched using an isotropically distributed background chlorine flux and inverse lag was observed for features etched with a molecular and atomic chlorine flux arriving directly from the effusive source. Microtrenching was also present in the etched features. Computer simulations of the etching process and profile development were performed using the kinetic model and a line-of-sight re-emission model for the chlorine transport. Using the simulation, atomic to molecular chlorine recombination effects were explored as a function of the surface recombination coefficient. Predictions of the simulations were compared to experimentally-derived profiles and were found to be in good agreement.

9:00am **PS-WeM3 Investigation through Simulation of the Effect of Ar Addition on the Cl@super +@/Cl@sub 2@@super +@ Ratio in Chlorine Discharges*, J. Helmsen,*** *P. Loewenhardt,* Applied Materials Inc.

.A cause of compromise in commercial Al etch processes that employ Cl discharges is the removal of Cu residue. This residue is due to the presence of Cu that has been added to the Al to prevent electromigration. Investigation of processes that successfully remove this residue have shown that the Cl@super +@/Cl@sub 2@@super +@ ratio measured near the wafer has been found to positively correlate with residue removal.@footnote 1@ This ratio can increase as a result of lower pressures and increased source powers, but also can increase due to the addition of Ar into the plasma. Investigation of the ratio through the use of simulation in pure Cl plasmas has shown the ratio is controlled by charge exchange between Cl@super +@ and Cl@sub 2@ producing Cl@sub 2@@super +@ and Cl.@footnote 2@ The proposed influence of Ar is dilution of Cl@sub 2@, thereby allowing a greater proportion of Cl@super +@ to not participate in the reaction and reach the surface. The effect is shown through the use of plasma simulation with the Hybrid Plasma Equipment Model (HPEM).@footnote 3@ @FootnoteText@ @footnote 1@ P. Loewenhardt, "Plasma Diagnostics: Use and Justification in an Industrial Environment", 51st Annual Gaseous Electronics Conference, Maui, Hawaii, Oct. 1998. @footnote 2@ J. Helmsen, D. Hammer, J. Yamartino and P. Loewenhardt, "Investigations of Rate Coefficients in the Cl Model", IEEE Transactions on Plasma Science (Accepted for Publication) @footnote 3@ P. L. G. Ventzek, M. Grapperhaus and M. J. Kushner, "Investigation of Electron Source and Ion Flux Uniformity Measurements in High Plasma Density Inductively Plasma Tools Using 2-Dimensional Modeling", J. Vac. Science Tech. B 12, 3118-3137 (1994)

9:20am **PS-WeM4 Does Mask Charging Influence Sidewall Trench Formation ?*, H.C. Lee,*** *G.S. Hwang,* California Institute of Technology*; H.S. Lee,* Hyundai Electronics Co. Ltd., Korea*; K.P. Giapis,* California Institute of Technology*; L. Desvoivres, L. Vallier, O. Joubert,* France Telecom-CNET, France

There has been some controversy in the etching community about how and to what extent charging effects influence profile evolution during the main etch in high-density plasmas. Microtrenching, for example, is believed to occur as a result of forward scattering of ions at the sidewalls. While charging is not essential for microtrenching, simulations have shown that mask charging could perturb the ion trajectories so that more ions scatter at the sidewalls; the resulting increase in scattered ion flux causes deeper microtrenches. This effect is difficult to prove when the mask is made of polymeric material because mask erosion influences the profile. Mask faceting, in particular, could increase the scattered ion flux to the trench bottom thereby dominating microtrench formation. It is then imperative that a hard mask be used to prevent any chemical or physical interference with trench profile evolution. We have performed a combined experimental and theoretical study of the contribution of mask charging to microtrenching. A Si wafer was patterned with gratings of hard oxide masks of linewidths down to 0.2 µm and then etched in a high-density, pure Cl@sub 2@ plasma to various depths. Three different mask thicknesses were tried: 0.2, 0.5, and 0.7 µm. Profile evolution simulations in the ion-limited regime predict that microtrenching should worsen with mask thickness because of increased scattering due to: 1) the larger sidewall area, and 2) ion deflection caused by upper mask sidewall charging. For mask aspect ratios larger than 3:1, charging of the lower part of the sidewall leads to an ion focusing effect that decreases significantly the microtrench depth resulting in rounded trench bottom profiles. While the experimental results generally support these trends, we find also important differences in the profile shapes. A side-by-side comparison will be shown and the charging contributions to microtrenching will be discussed.

9:40am **PS-WeM5 Modeling Feature Evolution in Plasma Processes*, D.B. Graves,*** University of California, Berkeley **INVITED**

Control of the shape of features during etching or deposition is central to the success of many plasma processes used for semiconductor manufacturing. Unfortunately, current models of feature shape evolution are relatively primitive with limited predictive capability. A major goal of plasma process modeling is to develop truly predictive feature shape evolution simulations. One reason for the difficulties experienced in developing predictive shape evolution models is that many parts of the plasma play a role. Events at the tool scale help to govern the composition, flux and energy of ionic and neutral species that impact substrates. The sheath and local presheath above the substrate play important roles in governing positive ion energy and angular distributions at surfaces. In some cases, electron energy distributions and negative ions can be important in feature differential charging phenomena. Features are themselves often complex, with materials and geometries that challenge current models. Processes within a feature, including neutral reaction, ion-sidewall scattering, sputtering, charge transport and redeposition of etch products are all potentially important. An important issue is the sensitivity of the predicted shape evolution to inaccuracies in various parts of the model. In this talk, I will review the progress in developing models of reactive plasma processes, focusing on the phenomena that are known or suspected to affect feature shape evolution. Predictive feature shape evolution models must include the tool scale, the sheath, the feature itself, as well as processes occurring at surfaces. I will review progress made in using vacuum beam experiments, atomistic simulations, and plasma experiments that focus on feature shape evolution. I will highlight the need for more systematic studies of plasma process feature shape evolution, the development of novel sensors, and the development of physically-based, phenomenological surface rate expressions.

10:20am **PS-WeM7 Feature Profile Evolution of SiO@sub 2@ Trenches in Fluorocarbon Plasmas***, **H.H. Hwang**,* Thermosciences Institute*; T.R. Govindan, M. Meyyappan,* NASA Ames Research Center*; V. Arunachalam, S. Rauf, D.G. Coronell,* Motorola

Etching of silicon microstructures for semiconductor manufacturing in chlorine plasmas has been well characterized. The etching proceeds in a two-part process, where the chlorine neutrals passivate the Si surface and then the ions etch away SiCl@sub x@. However, etching in more complicated gas mixtures and materials, such as etching of SiO@sub 2@ in Ar/C@sub 4@F@sub 8@, requires knowledge of the ion and neutral distribution functions as a function of angle and velocity, in addition to modeling the gas-surface reactions. In order to address these needs, we have developed and integrated a suite of models to simulate the etching process from the plasma reactor level to the feature profile evolution level. This arrangement allows for a better understanding, control, and prediction of the influence of equipment level process parameters on feature profile evolution. We are currently using the HPEM (Hybrid Plasma Equipment Model) and PCMCM (Plasma Chemistry Monte Carlo Model) to generate plasma properties and ion and neutral distribution functions for argon/fluorocarbon discharges in a GEC Reference Cell. These quantities are then input to the feature scale model, Simulation of Profile Evolution by Level Sets (SPELS). A surface chemistry model is used to determine the interaction of the incoming species with the substrate material and simulate the evolution of the trench profile. The impact of change of gas pressure and inductive power on the relative flux of CF@sub x@ and F to the wafer, the etch and polymerization rates, and feature profiles will be examined. Comparisons to experimental profiles will also be presented.

10:40am **PS-WeM8 Application of an Integrated Feature Scale Model to Ionized PVD of Cu Barrier and Seed Processes***, **V. Arunachalam**, D.G. Coronell, S. Rauf, P.L.G. Ventzek, X.-Y. Liu,* Motorola Inc.

Ionized PVD has emerged as an important process for the deposition of Cu barrier and seed films in high aspect ratio features. Experiments have shown that ionized PVD results in improved bottom and sidewall coverage owing to the highly anisotropic ion fluxes and the resputtering caused by the energetic ions respectively. Our, previous work@footnote 1@ described the analysis of a single deposition step as a seamless integration of equipment, sheath, feature and atomistic level phenomena. We have extended and improved upon our previous model to consider more detailed process issues at the feature scale level. In particular, we have developed a three-dimensional Monte Carlo-based surface moving algorithm capable of simulating the deposition of multi-component films and multiple deposition steps. In this presentation, we demonstrate the applicability of the model to address process integration and the compositional control of multi-component films. The importance of the initial feature geometry, the ability of the depositing material to wet the underlying substrate, and the preferential sputtering of one film constituent over another will be discussed. @FootnoteText@ @footnote 1@ D. Coronell et al. AVS 1998 paper

11:00am **PS-WeM9 Analysis and Simulation of Mask Erosion During Dry Etching***, **J. Westlinder**, F. Engelmark, L.B. Jonsson, C. Hedlund, I.V. Katardjiev, H.-O. Blom,* Uppsala University, Sweden

In order to do topography simulations, which is an important part of process simulation, the erosion/growth rates of materials exposed to different complex processes must be determined. The erosion of the mask during plasma etching is becoming increasingly important as the feature size continues to shrink. By using anisotropic wet etching of silicon wafers it is possible to create structures defined by specific crystallographic planes. This results in silicon groove structures consisting of 7-10 µm wide planar surfaces which form various angles with respect to the wafer normal. The structures can then be coated with different materials and processed under standard operating conditions. Since only Si wafers are used the method is fully IC production compatible and can be used directly in production systems. The method is used to analyze the erosion of different mask materials. Data for the angular dependence of the etch rate for different dry etching processes like e.g. RIE and ICP and for different mask materials used in IC manufacturing have been obtained and will be presented. The results are used as input data to the topography simulation software DINESE.

11:20am **PS-WeM10 Characterization of Photoresist Trimming in a Lam TCP9400 With the Aid of a Profile Simulation***, **V. Vahedi**,* Lam Research Corporation*; S Lin,* Lam Research Corporation, Taiwan*; H.W. Chang,* Lam Research Corporation*; H.J. Tao, C.C. Chen, C.S. Tsai, M.S. Liang,* Taiwan Semiconductor Manufacturing Company

As a result of the lithography limitations in printing photoresist lines below 0.18m, there is a growing interest in reducing the mask linewidth (in a controlled manner) using dry process tools. This process is called photoresist trimming. A typical polysilicon gate film stack for the next generation devices may include photoresist/hardmask/polysilicon/gate oxide. The advantage of photoresist trimming is that it can be done in situ and can be integrated into the process steps. In this paper, we will discuss the challenges and issues with this process. To accelerate the process development & optimization, we are using a profile simulator to understand the basic mechanisms. Typical trim processes include oxygen with other additives. Our proposed mechanisms for photoresist trimming include chemical etching, ion-enhanced etching & physical sputtering. These mechanisms are included in our profile simulation, and the simulation is calibrated with experimental data. We will show quantitative comparison between simulation and experiments. Once calibrated, the simulation can be used to predict profile changes for any line and spacing. The simulation is being used to study photoresist foot removal and CD variations between isolated and dense lines.

Surface Science Division

Room 606 - Session SS1-WeM

Surface Structure

Moderator: J. Hinch, Rutgers University

8:20am **SS1-WeM1 Temporal Diffraction: A New Method for Studying Surface Kinetics***, **E.H. Conrad**,* The Georgia Institute of Technology **INVITED**

An understanding of surface kinetics is crucial to many areas of 2D and 3D film growth. A variety of techniques are currently available to extract surface kinetics parameters such as diffusion coefficients, atom attachment rates to islands and steps, etc. Most of these techniques, however, are limited to low coverages (i.e., single atom kinetics) and a limited temperature range (usually far from equilibrium). We have been developing a new technique, Temporal LEED Spectroscopy (TLS), that should be applicable over a much larger range of temperatures and up to densities where hydrodynamic diffusion equations are applicable.@footnote 1@ This technique uses the inherent intensity fluctuations, @delta@I(t) = I(q,t)-*, in a surface diffraction experiment that are caused by the motion of steps, atoms, grain boundaries, etc. From these fluctuations a self auto-correlation function, G(@tau@)) = <@delta@I(t)@delta@I(t+@tau@)>, is constructed that contains the essential kinetics information. I will present a short discussion of how the technique works and the limits on its sensitivity and time resolution. As a specific example, I will show how kinetics information from a system of fluctuating steps on a vicinal surface can be extracted. Data will be presented for two systems where the step motion is governed by different rate limiting kinetics: stepped W(430) and stepped Si(111) surfaces. @FootnoteText@ @footnote 1@ E.H. Conrad, A. Menzel, S. Kiriukhin and M.C. Tringides, Phys. Rev. Lett. 81, 3175 (1998).*

9:00am **SS1-WeM3 Similarities in Tensile and Compressive Strain Relief in Growth of Cu and Ag on Ru(0001)@footnote 1@**, ***A.P. Baddorf,*** Oak Ridge National Laboratory; *H. Zajonz,* Brookhaven National Laboratory; *D.M. Zehner,* Oak Ridge National Laboratory; *D. Gibbs,* Brookhaven National Laboratory

Growth and dynamics of strained films of Cu and Ag on Ru(0001) have been studied at temperatures between 300 and 925 K using x-ray diffraction. A diverse series of structures are observed, which appear to be prevalent in heteroepitaxial growth on hexagonal surfaces. Thin films of both Cu and Ag are initially strained, in the first case from tensile stress of a 5.8% lattice mismatch and in the second from compressive stress of a 6.3% mismatch. Both Cu and Ag form stripe phase reconstructions, in which strain is reduced by uniaxial contraction or expansion along the [100] direction of the film. In Cu films, the stripe phase appears during formation of the second layer, the first being pseudomorphic, while in Ag films the first layer forms the stripe phase. For Cu, the stripe phase undergoes an abrupt incommensurate/commensurate transition to a registry dependant on temperature. Differences in thermal expansion may explain this temperature dependence. A second registry is correlated with third layer growth of Cu, however the third layer is metastable. At higher coverages, both Cu and Ag stripe phases coexist with (111) oriented 3-dimensional islands. For Cu, island formation follows stripe phase development, however for Ag, unstable islands appear first and participate in formation of the stripe phase. Structures grown in equilibrium at high temperature are compared with those grown at room temperature and imaged with scanning tunneling microscopy as well as with results from semi-empirical calculations. @FootnoteText@ @footnote 1@ORNL is managed by Lockheed Martin Energy Research Corp. under US DOE contract DE-AC05-96OR22464. BNL is supported by US DOE DE-AC02-98CH10886.

9:20am **SS1-WeM4 Step-Step Interactions on TaC(910)@footnote 1@**, *J.-K. Zuo,* Oak Ridge National Laboratory and Southwest Missouri State University; *T.-J. Zhang,* University of Tennessee and Oak Ridge National Laboratory; ***J.F. Wendelken****, Z. Zhang, D.M. Zehner,* Oak Ridge National Laboratory

TaC, an ionic crystal with an extremely high melting point of ~3983 C, exhibits a strong faceting behavior for (n10) surfaces after heating to ~2000°C.@footnote 2@ These facets are very regular when n = 1, 2 or 3 but become less regular when n = 9. Through a scanning tunneling microscopy based study of the step distribution and structure on TaC(910), we determine that the observed morphology results from the interplay of a step-step repulsive interaction with both short- and long-range attractive interactions. The surface is dominated by bunched double-height steps where the bunches are separated by relatively long intervening (100) terraces having irregular widths. The step-separation distribution is highly skewed and sharply peaked at 13 atomic rows, the average spacing within a step bunch, while the (910) orientation is maintained with an average step-separation of about 18 rows. A Monte Carlo simulation shows that a weak, long-range, attractive interaction, -B/x@super a@, must be added to a strong, medium-range, repulsive interaction, A/x@super 2@, to fit the measured distribution. In addition, a short range attractive interaction is required for the creation of multiple-height steps that are oriented in the [010] direction. Possible physical origins for each of these interactions will be discussed. @FootnoteText@ @footnote 1@ ORNL is managed by Lockheed Martin Energy Research Corp. under U.S. DOE Contract No. DE-AC05-96OR22464. @footnote 2@ J.-K. Zuo, J. M. Carpinnelli, D. M. Zehner and J. F. Wendelken, Phys. Rev. 53, 16013 (1996).

9:40am **SS1-WeM5 Phosphide Phases on Cu(001): a Helium Atom Scattering Study**, *L.V. Goncharova, J. Braun, A.V. Ermakov,* ***B.J. Hinch,*** Rutgers University

PF@sub 3@ and PH@sub 3@ adsorbs molecularly on Cu(001) at low surface temperatures. As these molecules are susceptible to electron induced decomposition; helium atom scattering proves to be a powerful diagnostic tool. On raising the surface temperature competition between desorption and decomposition occurs. Decomposition is complete after annealing to room temperature. A low coverage of phosphorous induces a poorly ordered c(6x8) phase. Subsequent annealing to 500K substantially improves the long range ordering of this structure. For PF@sub 3@ exposures at room temperature, no adsorption is observed. In contrast, PH@sub 3@ adsorbs dissociatively. Under these exposure conditions a c(6x6) phase is observed. Both c(6 x 8) and c(6 x 6) phases display low rainbow angles implying phosphorus incorporation into the surface plane. We shall discuss possible structures for these low-corrugation, phosphorus-in-copper phases.

10:00am **SS1-WeM6 Ordered Alloying of Pd with the Mo(001) Surface**, *D. Wu, Z.Q. He,* ***M.S. Altman,*** *W.K. Lau, C.T. Chan,* Hong Kong University of Science and Technology, P.R. China

The interaction of Pd with the Mo(001) surface has been studied with low energy electron microscopy (LEEM) and diffraction (LEED), and first principles total energy calculations. A significant change of surface morphology is revealed by LEEM during the development of a Pd-induced c(2x2) periodic structure. The creation of a large number of islands upon Pd deposition is consistent with the formation of a subsitutional alloy. Accommodation of Pd in excess of the ideal c(2x2) coverage leads to the formation of a c(2x8) structure, although with no apparent change of surface morphology. The c(2x8) structure is stable at the interface between Mo and thicker Pd overlayers. Theoretical calculations demonstrate that the substitutional alloy is energetically favored compared to an overlayer structure at half monolayer coverage. Proliferation of antiphase domain walls in the c(2x2) subsitutional alloy is proposed to explain the c(2x8) periodic structure. Theoretical calculations indicate that a pseudomorphic Pd overlayer is more stable than substitutional alloys at one monolayer coverage, and that the Pd-covered Mo(001) surface would be unstable with respect to faceting to the (112) orientation if the pseudomorphic growth can be realized. However, experiment reveals that there is a kinetic limitation to the formation of the pseudomorphic structure and that faceting is preempted by the formation of more complex surface alloy structures.

10:20am **SS1-WeM7 Alkali-Metal-induced 3x1 Reconstruction of the Ge(111) Surface**, ***G.S. Lee,*** Korea Research Institute of Standards and Science, Korea; *J. Kim,* Korea Advanced Institute of Science and Technologies; *I. Chizhov, H. Mai, R.F. Willis,* The Pennsylvania State University

We present the scanning tunneling microscopy (STM) images of the 3x1 reconstruction of the Ge(111) surface induced by the adsorption of Na and Li. Both filled- and empty-state images of Ge(111)3x1-Na consist of double-row zigzag chains. For Ge(111)3x1-Li, the filled-state image shows single-width rows with sparsely distributed block features between the rows, while the empty-state image is characterized by double rows of dimer-like features. For both surfaces, the dual-polarity images taken simultaneously reveal lateral shift and phase reversal of the rows upon polarity reversal. The apparent dissimilarity of the STM images is contradictory to the expectation that the Ge(111)3x1 surface, like the Si(111)3x1 surface, is a substrate reconstruction which is not specific to the kind of alkali metals. The interpretation of the images of both Ge(111)3x1 surfaces will be discussed by comparing with those of the Si(111)3x1 surfaces, and the recently proposed structural model for the Si(111)3x1 reconstruction.

10:40am **SS1-WeM8 High-Resolution Structural Analysis of Te/Ge(001)**, ***B.P. Tinkham,*** Northwestern University; *P.F. Lyman,* University of Wisconsin, Milwaukee; *O. Sakata, D.A. Walko,* Northwestern University; *M.J. Bedzyk,* Northwestern University, Argonne National Laboratory

We propose models for the surface structure of Te/Ge(001). Te has proven to be an effective surfactant for Si/Ge heteroepitaxy.@footnote 1@ Thus, the study of Te/Ge(001) will determine more precisely the method of surfactant action. Our group has performed high-resolution XSW (X-Ray Standing Wave) and LEED (Low-Energy Electron Diffraction) studies at Te coverages of 1 and .5 monolayer. We are presently investigating these structures with surface x-ray diffraction in order to allow us to fully describe the surface structure, including the composition and structure of the Te dimers. STM will also be used to verify the competing models suggested by the x-ray measurements. @FootnoteText@ @footnote 1@ H.J Hosten, J. Klatt, G. Lippert, E.Bugiel, and S. Higuchi, J. Appl. Phys. 74, 2507 (1993).

11:00am **SS1-WeM9 A Novel STM Imaging Mechanism Used to Resolve the Atomic Structure of the As-Rich GaAs(001)-(2x4) Surface**, ***V.P. LaBella,*** *D.W. Bullock, P.M. Thibado,* University of Arkansas; *P. Kratzer, M. Scheffler,* Max-Planck-Gesellschaft, Germany

Motivated by the importance of GaAs in the compound semiconductor device market. The atomic arrangement of the technologically important GaAs(001)-(2x4) reconstructed surface is determined using scanning tunneling microscopy (STM) and first-principles, electronic structure calculations. The bias-dependent STM images reveal the relative position and depth of atomic-scale features within the trenches between the top layer As dimers, which are in agreement with the @beta@2 (2x4) structural model. The bias-dependant simulated STM images reveal that a retraction of the top most dangling bond orbitals is the unique mechanism that enables the STM tip to image the trench structure. This work was funded in part by the National Science Foundation (DMR-9733994) and the Office of Naval Research (N00014-97-1-1058).

11:20am **SS1-WeM10 Dislocations, Phason Defects, and Domain Walls in a One-dimensional Quasiperiodic Superstructure of a Metallic Thin Film***, Ph. Ebert,* Forschungszentrum J@um u@lich, Germany*; K.-J. Chao, Q. Niu,* ***C.K. Shih,*** University of Texas, Austin

We investigated disorder and structural defects in a one-dimensional quasiperiodic superstructure of a thin Ag film on GaAs(110) surfaces by scanning tunneling microscopy. The superstructure forms sequences with long and short separations exhibiting a self-similarity. We demonstrate that the modulation can be described best with a Fibonacci sequence and deviations are due to structural defects. We identify dislocations, phason defects, and domain walls. The static stress field of dislocations is found to be a source of phason defects.

11:40am **SS1-WeM11 The Surface Reconstructions of InP(001)***,* ***Z. Ding,*** *V.P. LaBella, D.W. Bullock, P.M. Thibado,* University of Arkansas

Motivated by the increasing use of InP in high speed opto-electronic devices that are fabricated using molecular beam epitaxy (MBE), the surface reconstruction phases of the technologically important InP(001) surface are studied. This study is performed in a combined ultrahigh vacuum MBE and scanning tunneling microscopy (STM) multi-chamber facility that incorporates a solid source phosphorus evaporation source and a novel temperature measurement system accurate to within ±2 @super o@C. Both reflect ion high energy electron diffraction (RHEED) and STM are used to map out the InP(001) surface reconstruction phase's dependence upon substrate temperature and phosphorus pressure. A c(4x4), a (2x1), and a (2x4)/c(2x8) reconstruction are all observed. Thi s work was funded in part by the National Science Foundation (DMR-9733994) and the Office of Naval Research (N00014-97-1-1058).

Surface Science Division

Room 607 - Session SS2+AS+PS-WeM

Ion-Surface Interactions I

Moderator: L. Hanley, University of Illinois, Chicago

8:20am **SS2+AS+PS-WeM1 Trapping and Desorption of Energetic Cu Atoms on Cu(111) and (001)Surfaces at Grazing Incidence***,* ***D.E. Hanson,*** *A.F. Voter, J.D. Kress,* Los Alamos National Laboratory*; X.-Y. Liu,* Motorola, Inc.

Cu is widely used as an interconnect in semiconductor chips. It is deposited by ionized physical vapor deposition on sub-micron features that have sidewalls nearly parallel to the incident ion beam. Molecular dynamics (MD) simulations have shown that, for angles of incidence (with respect to normal) up to 20 degrees, the sticking probability is unity for all energies; the impact atom penetrates and loses all of its kinetic energy to the surface. As the impact angle increases, the probability for the impact atom to reflect increases, reducing the sticking probability. Surprisingly, for angles above 70 degrees, the sticking probability increases with impact angle. We have performed MD simulations of Cu atoms impacting both Cu(111) and (001) surfaces at grazing incidence and find that this unexpected increase in sticking probability is a consequence of trapping (or surface skipping). An energetic Cu atom (10 ¾ E ¾ 100 eV) can become trapped by the mean attractive potential above the surface, oscillating normal to the surface. While in this trapped state, it can traverse hundreds of Å as it dissipates energy to the surface. Until the atom either desorbs or comes to rest, it experiences an average energy loss rate that is piecewise linear, typically comprised of two or more roughly linear (dE/dt = constant) regions. The process can be characterized by two parameters: the desorption probability at each oscillation and an average energy loss rate (per oscillation) that is independent of energy. These parameter values are the same for both the (111) and (001) surfaces. A phenomenological model based on these parameters is presented, and the predictions of sticking probability, average energy transfer to the surface, and total distance traveled along the surface, agree with full MD simulations. The dependence of the desorption probability on the surface temperature, was also studied.

8:40am **SS2+AS+PS-WeM2 Dynamics of NO@super +@ Abstraction of Oxygen on Al(111)***,* ***M. Maazouz,*** *P.L. Maazouz, D.C. Jacobs,* University of Notre Dame

Energetic collisions between molecules and surfaces can activate a number of reaction processes, such as electron transfer, activated dissociative chemisorption, dissociative scattering, atom abstraction, and sputtering. The branching into each of these channels can be affected by the initial internal energy (electronic, vibrational, and rotational) and collision energy of the molecule. Reactive collisions of NO@super +@(@Chi@ @super 1@@Sigma@@super +@, v=1) with oxygen-covered Al(111) are explored across a range of hyperthermal energies (5-80 eV). A laser forms the incident ions from the neutral NO via resonance-enhanced multiphoton ionization (REMPI). This produces NO@super +@(@Chi@ @super 1@@Sigma@@super +@, v) in a selected vibrational level (v=0-6) of the ground electronic state. Scattered products include O@super -@, NO@super -@, and NO@sub 2@@super -@. The latter product arises from an atom abstraction channel and is the main focus for the present study. The NO@sub 2@@super -@ formation shows a strong dependence on the oxygen coverage and the NO@super +@ primary energy. Detailed reaction mechanisms leading to NO@sub 2@@super-@ emergence will be discussed.

9:00am **SS2+AS+PS-WeM3 Oxygen Negative Ion Emission from Al(100) Bombarded by Li@super+@ Ions***,* ***J.A. Yarmoff,*** *W.K. Wang, B.-L. Young, B.C. Corbitt,* University of California, Riverside*; Z. Sroubek,* Academy of Sciences of Czech Republic

The intensity of oxygen negative ions sputtered from metal surfaces (V, Mo, Cu) by rare gas ions is known to increase by up to 3 orders of magnitude when the surface work function is lowered by alkali metal adsorption. A resonant charge transfer process from the surface bands to the oxygen affinity level is apparently responsible for the negative ion formation, and such a process is strongly dependent on the surface potential. We have measured the intensities and kinetic energy distributions of O@super-@ sputtered from Al(100) via bombardment by 200 eV Li@super+@ ions. In contrast to experiments with rare gas ions, the O@super-@ intensity is found to be relatively independent of the work function changes induced by Cs deposition (@DELTA@@phi@ = - 3 eV). For O@super-@ kinetic energies above 20 eV there is no increase in the yield, and it increases by only a factor of 2-3 at lower O@super-@ kinetic energies. The energy distribution depends exponentially upon the O@super-@ kinetic energy, and has a cutoff at about 120 eV. These results suggest that the yield of oxygen particles sputtered from clean Al(100) by Li@super+@ is already nearly completely ionized due to the local potential perturbation caused by the projectile. Thus, a further lowering of the surface potential by the deposition of alkali adsorbates has little effect. This is clear evidence of the localized nature of the resonant charge exchange process, and the first evidence that such a local effect can be induced by the primary particle.

9:20am **SS2+AS+PS-WeM4 Matrix Dependent He+ Neutralization by Adsorbates: An ISS Study of S and Cl on TiO@sub 2@(110)***,* ***W. Hebenstreit,*** *E.L.D. Hebenstreit, U. Diebold,* Tulane University

We have studied the adsorption of S and Cl on TiO@sub 2@(110) with low-energy He@super +@ ion scattering spectroscopy (ISS) , X-ray photoelectron spectroscopy (XPS), and scanning tunneling microscopy (STM). Because of its high surface sensitivity, ISS is ideally suited to determine the chemical composition of surfaces. While it is well known that quantification of ISS spectra is influenced by trajectory-dependent blocking, the element-specific neutralization of the probing ion is generally assumed not to be matrix dependent. We found that the neutralization of He+ ions (400 - 2450 eV, scattering angle 139°) scattered on Cl or S (adsorbed on TiO@sub 2@(110)), depends strongly on sample pretreatment and adsorption site. Cl (~ 1 ML) and S (~ 2/3 ML) give rise to pronounced peaks in ISS spectra when adsorbed on the sputtered TiO2 sample (1 keV Ar@super +@, flux 1.5 10@super 16@ cm@super -2@), but both species cannot be detected after adsorption at RT on the annealed, stoichiometric TiO@sub 2@(110) surface (coverage ~ 1/3 ML). STM shows that the adsorbates are located on the rows of 5-fold coordinated Ti atoms. When dosed at 573 K, S adsorbs at the position of bridging oxygen atoms, where it forms a (1x3) superstructure. In this case S becomes "visible" again for ISS. All spectra (on sputtered and annealed substrates) show a decrease in the O and Ti ISS signal due to blocking induced by the adsorbates. Subsurface positions of the adsorbates in the "invisible cases" can be excluded by STM. The difference in neutralization is due to different electronic structures of the substrate surface: (a) semiconducting with a 3 eV band gap when annealed; (b) metallic due to defect states and oxygen deficiency after sputtering. In case of S located at the position of bridging oxygens, neutralization is affected by the different local bonding.

9:40am **SS2+AS+PS-WeM5 Hyperhherthermal Ion - Surface Interactions*, J.W. Rabalais,*** University of Houston **INVITED**

The chemical and physical phenomena accessible by means of low energy ion beams on surfaces will be discussed. Such energetic reactive ions can stimulate selected physical and chemical processes, such as film deposition, growth, synthesis, and shallow implantation within a nonequilibrium UHV environment. The 'low energy' or 'hyperthermal' range is considered to be 5 eV to a few keV. The lower limit is of the order of chemical bond energies. In this limit, chemical bonding interactions become significant, the binary-collision approximation (BCA) becomes questionable, and inelastic interactions can alter the ion trajectories. In the high energy limit, the sputtering yield becomes equivalent to or higher than the beam flux, classical ion trajectory simulations using the BCA provide a satisfactory description of the collision events, and the impinging ions are implanted in the subsurface layers. Mass-selected ion beam deposition (IBD) allows independent control over parameters such as ion energy and type, ion fluence and dose, substrate temperature, and background gases. The advantages of IBD for stimulation of chemical reactions, control of film stoichiometry, low temperature epitaxy, good film-substrate adhesion, and for growth of materials with metastable structures, isotopic purity, and high densities will be contrasted with the disadvantages, such as production of defects, imperfections, and amorphous materials and the limited thicknesses of IBD films. Examples of the use of mass- and energy-selected beams for hyperthermal surface reactions, film growth, synergism between ion energy and substrate temperature, and shallow implantation will include: Si+ ion homoepitaxy, the growth SiO2 from pulsed Si+ and O+ beams, low energy Ti+ beams for growth of titanium silicide on silicon and mixed Ti-Al oxides on sapphire (a-Al2O3), growth of diamond-like carbon, growth of Ag(111) on a Ni(100) surface, and survival probabilities of scattered TiClx cluster ions.

10:20am **SS2+AS+PS-WeM7 Dissociation and Energy Distribution Processes in XY@super -@(CO@sub 2@)@sub n@ (XY = ICl, I@sub 2@, and Br@sub 2@) Collision onto Silicon Surface*, S. Koizumi,*** Genesis Research Institute, Inc., Japan*; H. Yasumatsu, A. Terasaki, T. Kondow,* Toyota Technological Institute, Japan

Collisional dissociation induced by impact of a cluster anion, ICl@sup -@(CO@sub 2@)@sub n@ (n = 0 - 20), onto a silicon surface were studied by measuring the branching fractions of the ICl@sup -@ dissociation and the translational energies of the product anions as functions of n and the collision energy (per ICl@sup -@) of ICl@sup -@(CO@sub 2@)@sub n@ in an apparatus consisting of a tandem time-of-flight mass spectrometer. It was found that the branching fraction of the ICl@sup -@ dissociation did not change with n at the collision energies of 30 - 70 eV. Molecular dynamics simulation showed that the impinging core ion, ICl@sup -@, tends to orient with the molecular axis of the core ion being at the angle of 55 ° with respect to the surface normal, whereas in the X@sub 2@@sup -@(CO@sub 2@)@sub n@ (X = Br, I) collision, the molecular axis of the X@sub 2@@sup -@ core ion being in parallel to the surface plane. This finding together with prominent wedge effect in the X@sub 2@@sup -@(CO@sub 2@)@sub n@ collision leads us to conclude that the CO@sub 2@ molecules do not work as 'wedge' in the ICl@sup -@(CO@sub 2@)@sub n@ collision because of the unfavorable orientation of the incoming cluster anion. No discernible cage effect could also be related to the orientation. The translational energies of the product anions were interpreted in terms of energy redistribution of the collision energy among the degrees of freedom of the cluster anion and the surface atoms involved in the collision. It was also found that the I and Cl product ions reach quasi-equilibrium with the surface from the measurement of these translational energy distributions.

10:40am **SS2+AS+PS-WeM8 Angle Resolved Measurements of Ions and Neutrals Scattered from HOPG Surfaces upon Hyperthermal Glancing Incidence Irradiation with Large Polyatomic Ions: Charge Changing and Impact Orientation Phenomena***, M. Hillenkamp, J. Pfister,* ***M. Kappes,*** University of Karlsruhe, Germany*; R. Webb,* University of Surrey, United Kingdom

We have scattered a series of polyaromatic hydrocarbons and various fullerenes from graphite at hyperthermal kinetic energies (100-5000eV) under glancing incidence (75 degrees with respect to the surface normal). Resulting cations, anions and fast neutrals have been studied with a secondary time-of-flight mass spectrometer/detector rotatable about the scattering plane. The corresponding angular distributions have been compared to those obtained upon irradiation of HOPG with He@super +@ and Xe@super +@ ion beams under otherwise identical conditions. Molecular projectiles were typically studied as either singly or multiply charged parent cations. In addition to dominant neutralization, we also observe the scattering of smaller amounts of both cations and anions (parents and fragments). We discuss the relative yields of charge states in terms of charge transfer rate theories as well as in terms of postcollision decay processes (e.g. delayed electron loss). In comparing the surprisingly narrow (and near Gaussian) angular distributions determined for fast neutrals from fullerene scattering with those recorded for xenon, we find that while Xe is specularly scattered over the full energy range studied, fullerenes are scattered subspecularly - with the deviation from specular angle increasing with increasing collision energy. Molecular dynamics simulations with Brenner potentials suggest that this effect results from a combination of the comparatively long (>300 fesec) "turnaround " time of the molecular projectile and a significant perpendicular deformation of the layered target on the collision time scale. For the topologically much more anisotropic polyaromatic hydrocarbon projectiles we find structured fast neutral angular distributions suggestive of a simple dependence between impact orientation and scattering angle

11:00am **SS2+AS+PS-WeM9 Surface Structure Determination by Angle-Resolved Mass Spectroscopy of Recoiled Ions*, G.S. Herman,*** Pacific Northwest National Laboratory

Low energy ion scattering (LEIS) and direct recoil spectroscopy (DRS) are powerful techniques for the determination of surface composition and structure. The combination of time-of-flight methods with an electrostatic time focussing analyzer has recently resulted in a new technique - mass-spectroscopy of recoiled ions (MSRI).@footnote 1@ The MSRI technique has an advantage over LEIS and DRS in that it has much higher mass-resolution and sensitivities. Results related to the exchange of @super 18@O into samples will be presented to illustrate the high mass-resolution. Furthermore, recent results indicate that in the angle-resolved mode, structural determinations can be performed. Angle-resolved MSRI (AR-MSRI) results will be presented for CeO@sub 2@(001) and TiO@sub 2@(001)-Anatase films grown on SrTiO@sub 3@(001) substrates by molecular beam epitaxy and chemical vapor deposition, respectively. The experimental data are fit to calculations using the scattering and recoiling imaging code based on the binary collision approximation.@footnote 2@ The ideal CeO@sub 2@(001) surface is polar and predicted to be unstable. However, LEED results indicate that a sharp (1x1) pattern can be obtained. The structural model determined by AR-MSRI consists of an oxygen-terminated surface with a half monolayer of oxygen removed. This structure is consistent with a model based on the reduction of the surface dipole moment. The TiO@sub 2@(001)-Anatase surface has only recently been experimentally investigated in much detail. LEED measurements indicate that the surface undergoes a (1x4) reconstruction after a sputter and anneal cycle. A comparison between experiment and theory for several models for this reconstruction will be presented. @FootnoteText@ @footnote 1@ K. Eipers-Smith, K. Waters, and J.A. Schultz, J. Am. Ceram. Soc. 76, 284 (1993). @footnote 2@ V. Bykov, C. Kim, M.M. Sung, K.J. Boyd, S.S. Todorov, and J.W. Rabalais, Nucl. Instr. And Meth. In Phys. Res. B 114, 371 (1996).

11:20am **SS2+AS+PS-WeM10 Depth Information in Direct Recoiling Peak Shapes: Simulations from Model Surfaces*, M. Tassotto,*** Oregon State University*; P.R. Watson,* Oregon State University, U.S.

Direct recoil spectrometry (DRS) has been used in the past to study adsorbate surface structures, chemisorption processes, and average orientations of molecules at surfaces. In these studies, DRS has experimentally been proven to be very surface sensitive. Information on surface structure and composition is primarily based on the analysis of DR peak intensities from the time-of-flight (TOF) spectra. These DR peaks frequently exhibit long tails to higher TOF which often overlap with neighboring peaks. It is common practice to obtain intensities from TOF spectra by integrating the DR peak areas over narrow time windows. Unfortunately, quantitative analysis is complicated by a lack of accurate background removal and only the use of relative intensity variations is possible. In this study, the MARLOWE computer code has been applied to calculate the trajectories of atoms recoiling from both simple and more complex model surfaces (diamond and alkane polymers, respectively) while the depth from which recoiled particles originated was recorded. The DR peak itself as well as the long TOF tail to lower energies contain depth-related information. Near the peak maximum recoils originate from mainly the first atomic layer, supporting the high surface sensitivity of DRS. The initial portions of the tail of the peak provide an approximate atomic depth profile but at longer TOF the tail contains recoils that were produced by several mechanisms from a wide variety of depths. The trajectory calculations have been converted to actual TOF spectra which allows comparison with experimental data from the literature. Here it is important to account for varying detector efficiencies as well as broadening of the simulated DR peak due to the finite pulse width of the ion beam. The MARLOWE calculations make DR peak deconvolution possible. This leads to accurate background removal in determining atomic ratios.

11:40am **SS2+AS+PS-WeM11 Hyperthermal-energy Ion Scattering on Si(100)*, C.L. Quinteros*,** *S.I. Tzanev, D.C. Jacobs,* University of Notre Dame

Ion-surface scattering experiments on a Si(100) surface are presented, introducing a new gas/surface experimental system with unique capabilities. Using a Colutron type source, an ion beam with energies between 5-300 eV can be generated. The ions are extracted, accelerated, mass-selected by a Wein filter, decelerated and focused on the surface target. Scattered ions and neutral products are mass- and energy-resolved with a fully rotatable, differentially-pumped detector that includes an ionization source for detection of neutrals, a cylindrical electrostatic analyzer for energy selection, and a quadrupole mass spectrometer for mass selection of the energy-filtered particles. Incident angles between 0-90° and scattering angles between 0-150° can be accessed by independent rotation of the sample manipulator and the detector. A complement of surface analysis techniques (LEED, Scanning Auger Electron Spectroscopy, X-Ray Photoelectron Spectroscopy, and a Kelvin Probe) monitor surface modifications resulting from ion-beam exposure. The surface sample can be cooled to 80K through a liquid nitrogen reservoir or resistively heated to 1000K. The hyperthermal energy range spans from thermal energies (<1eV), where chemical interactions produce inelastic scattering events, to the low energy regime (1-5 keV), where predominantly elastic scattering occurs. We present scattering results for a series of different projectiles on Si(100) that bridge these two energy regimes. The charge state and energy distributions of the scattered products are reported as a function of collision energy and scattering angle.

Surface Science Division
Room 604 - Session SS3+EM-WeM
Surface Electronic Structure

Moderator: G.O. Sitz, The University of Texas, Austin

8:20am **SS3+EM-WeM1 Spectroscopic Nonlinear Optical Responses of Clean, H-terminated and Ge-covered (2x1)Si(001)*, L. Mantese*,** *D. Lim, M.C. Downer,* University of Texas, Austin

Nonlinear optical spectroscopies are becoming important in elucidating the electronic structures of surfaces and interfaces. Yet, the accurate theoretical calculation of these spectra remains a difficult challenge. Recently, theoretical models have been developed to predict the nonlinear optical responses of clean and absorbate-covered (2x1)Si(001) surfaces.@footnote 1,2@ Here, we report the second harmonic (SH) responses of clean, H-terminated and Ge-covered (2x1)Si(001) to provide a direct test of predictive models. We have extended the range of previously reported results@footnote 3,4@ further into the IR where tunable IR femtosecond pulses in the range of ~1.15 to 2.5 microns were generated by a commercially available optical parametric amplifier (OPA) system. In this excitation region the SH response is resonantly enhanced by surface states including those from the dangling bonds and reconstruction-induced bonds. In addition, by directly using our oscillator output (700 to 800nm), we measure nonlinear optical responses in the E@sub 1@ region of Si. In this spectral range the SH response is highly sensitive and is altered in contrasting ways to ML coverages of H and Ge on (2x1)Si, originating from a surface electric field related to dimer charge transfer. The two measurement regions are discussed in comparison with theoretical predictions. @FootnoteText@ @footnote 1@B. Mendoza et al., PRL 81 (1998) 3781. @footnote 2@V.I. Gavrilenko et al., PRL submitted (1999). @footnote 3@U. Hofer, Appl. Phys. A 63 (1996) 533;J.I. Dadap et al., PRB 56 (1997) 13367. @footnote 4@P. Parkinson et al., Appl. Phys. B 68 (1999) 1.

8:40am **SS3+EM-WeM2 Si Surface Passivation: Si(111):GaSe versus Si(111):As*, A. Bostwick*,** *S. Meng, B.R. Schroeder,* University of Washington*; E. Rotenberg,* Lawrence Berkeley National Laboratory*; F.S. Ohuchi, M.A. Olmstead,* University of Washington

Heteroepitaxy on Si(111)7x7 requires removal of the deep reconstruction and accompanying dangling bonds. One way to passivate the Si(111) surface and remove the reconstruction is exposure to As, forming Si(111):As 1x1.@footnote 1@ The initial chemisorption of GeSe on Si(111)7x7 surfaces also results in a nearly ideally terminated 1x1 surface, quite similar to Si(111):As. Ga and Se occupy bulk Si sites, with Ga directly above Si (T1 site) and Se forming three back-bonds to Ga (H3 site). This (1x1) structure is the same as half a bulk GaSe layer, and initiates GaSe heteroepitaxy on Si(111). The very small (less than 0.1 eV) Si 2p core level shift shows the interface silicon to be in a bulk-like environment with minimal charge transfer, in contrast to As terminated silicon (0.75 eV shift). Electron counting arguments predict a lone-pair state on the Si(111):GaSe 1x1 surface, very similar to the As case. We observe such a state with angle-resolved ultraviolet photoemission spectroscopy. It has a similar E(k) dispersion to Si(111):As, though a somewhat larger bandwidth. We find a second surface state between this lone-pair state and the first bulk state, which we attribute to Ga-Se bonds. In addition, the zone-center bulk state, degenerate in bulk Si, is split by about 0.5 eV. This surprising result is not found for Si(111):As. We tentatively attribute the splitting to the Si-Ga interaction. @FootnoteText@ M. A. Olmstead, R. D. Bringans, R. I. G. Urhberg and R. Z. Bachrach, Phys. Rev. B 34, 6401 (1986).

9:00am **SS3+EM-WeM3 Electron Excitations and Optical Properties of Semiconductor Surfaces*, S.G. Louie*,** University of California, Berkeley and Lawrence Berkeley National Laboratory **INVITED**

The presence of electronic surface states and resonances often strongly modifies the structural, chemical, electronic, and optical properties of a surface. Over the past two decades, many sophisticated experimental methods (e.g., photoemission, scanning probes, and optical techniques) have been developed to investigate the spectroscopic properties of surfaces. In this talk, we discuss some of the theoretical developments in studying surface spectroscopic properties. Ab initio quasiparticle calculations can now be used to understand and predict surface-state excitation spectra such as those measured in photoemission and scanning tunneling spectroscopy experiments. A recent advance in treating excitonic effects further allows the first-principles study of surface optical processes. Results on several semiconductor surfaces will be presented. The possibility of using NMR chemical shifts as a probe of surface states will also be discussed.

9:40am **SS3+EM-WeM5 Low Temperature Scanning Tunneling Microscopy and Spectroscopy of the @sr@3x@sr@3 R30° Phase of Sn/Si(111)*, L. Ottaviano*,** INFM, Italy*; A. Continenza, M. Crivellari, L. Lozzi,* University of L'Aquila and INFM, Italy*; S. Modesti,* University of Trieste and Laboratorio TASC-INFM, Italy*; S. Picozzi, G. Profeta, S. Santucci,* University of L'Aquila and INFM, Italy

In these years there has been a great deal of efforts in the understanding of the low temperature transition from a @sr@3x@sr@3 R30° to a 3x3 phase of Sn(Pb)/Ge(111).@footnote 1@,@footnote 2@ On the other hand, little attention has been devoted to the investigation of iso-electronic interfaces like Sn(Pb)/Si(111) at similarly low temperatures. Among other experimental techniques, STM can provide a deep understanding of the electronic structure of these surfaces by performing measurements at various tunnelling voltages. Theorist who proposed different model interpretations have recently called for STM experiments at low temperatures on such systems.@footnote 3@ We show the first STM atomically resolved images of the low temperature (100 K) 1/3 ML-Sn/Si(111) @sr@3x@sr@3 R30° phase. Correspondingly we have measured tunnelling I-V spectra. Data are compared with all electron ab-initio calculations performed on a slab of Si(111) covered with 1/3 ML-Sn in the @sr@x@sr@3 R30° reconstruction. In particular we compare the ab-initio results with surface and electronic properties as obtained by STM/STS and photo-emission results. @FootnoteText@ @footnote 1@ L.Petaccia, L.Grill, M. Zangrando, and S. Modesti, Phys. Rev. Lett. 82 (1999) 386. @footnote 2@ A. Mascaraque et al., Phys. Rev.Lett. 82 (1999) 2524. @footnote 3@ S. Scandolo, F. Ancilotto, G.L.Chiarotti, G. Santoro, S. Serra, and E.Tosatti, Surf. Sci. 402-404 (1998) 808.

10:00am **SS3+EM-WeM6 Electronic Structure of the 3C-SiC(001)-c(4x2) Surface*, L. Duda*,** *L.S.O. Johansson, B. Reihl,* Universität Dortmund, Germany*; H.W. Yeom,* University of Tokyo, Japan*; S. Hara, S. Yoshida,* Electrotechnical Laboratory Tsukuba, Japan

We provide the first investigations of the electronic structure of the Si-rich 3C-SiC(100)-c(4x2) surface using angle-resolved photoemission and synchrotron radiation. The surface is found to be semiconducting. The Fermi level position was determined to be at 1.9 eV above the valence-band maximum. Three surface states are identified within the bulk band gap. We measured the dispersion of these states along the high-symmetry directions of the surface Brillouin zone (SBZ). The upper band at 1 eV binding energy and the third band at 2.6 eV are non-dispersive. The second band is located at 1.5 eV at the center of the SBZ and shows a weak dispersion of 0.3 eV in the @Gamma@-X direction, whereas, it is dispersionless in the other directions. We compare these results to calculated band structures.@footnote 1@ In addition, the comparison with experimental observed band structures of the 2x1 surface@footnote 2@ gives important new insight into the reconstruction behaviour of the SiC surface, supporting the close similarity of both reconstructions. @FootnoteText@ @footnote 1@ W. Lu, P. Krüger, J. Pollmann, Phys. Rev. Lett. 81 (1998) 2292 @footnote 2@ L. Duda, L. S. O. Johansson, B. Reihl, H. W. Yeom, S. Hara, S. Yoshida, submitted to Surface Science (1999).

10:20am **SS3+EM-WeM7 Photoemission Spectroscopy of Platinum Overlayers on Silicon Dioxide Films**, ***J.W. Keister***, *J.E. Rowe,* Army Research Office*; J.J. Kolodziej, T.E. Madey,* Rutgers University

Soft x-ray photoelectron spectroscopy has been used to study ultrathin Pt films on silicon dioxide as model supported-catalyst materials. Using monochromatic synchrotron radiation (NSLS U4A - Brookhaven), platinum and silicon core-level photoelectron peaks were measured as a function of platinum coverage in the range, 0 - 10 monolayers (ML). The bulk Si and SiO@sub 2@ film Si(2p) peaks both show a binding energy drop within the first ~ 0.5 ML of dosing. However, the effect is stronger for the SiO@sub 2@ film Si(2p) peak, indicating an increased screening of the 2p electrons by the metal overlayer. We also observe a monotonic increase of the Pt film workfunction with coverage from 4.52 eV initially to 5.59 eV at ~ 10 ML. The Pt(4f) and valence band spectra display changes with Pt dose which are also consistent with increased screening, from non-metallic below ~ 0.5 ML to metallic as coverage increases. The Pt core level decreases its binding energy from ~ 72.2 eV to ~ 70.9 eV between 0 and 10 ML coverage. The coverage dependence of the Pt lineshape and intensity, and the large saturation coverage for the workfunction change indicate cluster growth (Volmer-Weber growth). The increasingly metallic nature of the Pt overlayer with dose is quantified by numerical lineshape fitting with Gaussian-broadened Doniach-Sunjic functions, as appropriate for varying amounts of metallic screening. Further quantitative results and interpretation in terms of nucleation and growth of Pt clusters will be discussed.

10:40am **SS3+EM-WeM8 The Behavior of Metallic Quantum Well State Dispersions in the Cu/fccCo/Cu(100) System as a Function of Film Thickness***,* ***W.K. Siu,*** *R.A. Bartysnki,* Rutgers University

The magnetic coupling of ferromagnetic (FM) layers separated by a nonmagnetic (NM) layer has been associated with the formation and behavior of metallic quantum well (MQW) states in the spacer layer. Inverse photoemission has been used to investigate the MQW states in the prototypical Cu/fccCo/Cu(100) system for very thin Cu layers. These studies have shown that their dispersion with parallel momentum can be strongly affected by the electronic structure of the underlying FM material. Specifically, rapidly dispersing MQW states in the NM layer will acquire an uncharacteristically large effective mass when they encounter a projected band gap in the FM material. The experimental result shows the the behavior over severval Cu monolayers. In the Cu/fccCo/Cu(100) case, this occurs near the neck of the Cu Fermi surface and affect the states responsible for the short period coupling in this system. We have investigated how the dispersion of these levels develops as a function of Cu layer thickness and, in particular, how it evolves towards the behavior found for the single crystal Cu(100) surface. These results are explained in terms of a phase accumulation model for the electronic structure of the MQW system. Funded by the National Science Foundation under grant No. NSF-DMR98-01681. and the Petroleum Research Fund under grant No. ACS-PRF-33750-AC6,5.

11:00am **SS3+EM-WeM9 Atomic and Electronic Structure of Ag/Ni(110) and Ni/Ag(100)**, *P.T. Sprunger,* ***D.A. Hite,*** Louisiana State University

The atomic and electronic structure of Ag on Ni(110) and Ni on Ag(100) has been studied by synchrotron-based angle-resolved photoemission spectroscopy (ARUPS), low energy electron diffraction and scanning tunneling microscopy. These systems are of interest due their high bulk lattice mismatch and immiscibility. STM results of the Ag/Ni(110) system have revealed a novel pseudomorphic, surface-confined alloy phase at a coverage of ~0.5 ML. ARUPS results of this phase show a bulk-like, 3-D Ag electronic structure due to strong hybridization with the Ni bands. However, at a coverage of 1 ML, the Ag "de-alloys" and structurally forms a strained ~ Ag(111) overlayer. The electronic structure of this phase is radically different, namely, the laterally localized Ag d-bands show only k-parallel dispersion, that is, 2-D structure. In contrast, ARUPS results of Ni monolayer deposition on Ag(100) reveals no alloy formation below 150 K. However, at deposition temperatures above 400 K, Ni segregates subsurface, resulting in a Ag surface termination. The underlying Ni adopts Ag lattice parameters. ARUPS data from this latter phase reveals 3-D, bulk-like electronic structure due to strong mixing of states. The results will be compared and contrasted with theoretical band-structure calculations. This research is funded by DOE through contract DE-FG-02-98ER45712.

11:20am **SS3+EM-WeM10 Spin-Orbit-Split Surface States in Clean and Alkali-Metal-Covered W(110)@footnote 1@***,* ***E. Rotenberg,*** Lawrence Berkeley National Laboratory*; J.W. Chung,* Pohang Institute of Science and Technology, Korea*; S.D. Kevan,* University of Oregon

The broken symmetry at surfaces can give rise to a non-zero spin-orbit splitting of valence bands, as has recently been observed for the s-p derived surface state on Au(111).@footnote 2@ We now observe such a splitting of the d-derived surface state on W(110) and to a lesser extent, on Mo(110), and follow the evolution of the splitting as monovalent atoms are adsorbed. We find a dramatic increase in the splitting as a function of deposition for H and all alkali metals for coverages up to 1 ML. For Li, which shows the strongest change in splitting, we find a decrease in the splitting at the highest coverages near 1 ML. Our findings show that the spin-orbit splitting is a sensitive probe of the local surface conditions, to the extent that they are sampled by the surface state's wavefunction. The observed evolution is also directly relevant to recent observations of altered orbital magnetic structure vs. adsorbate coverage in magnetic materials. We propose a spin ordering for the associated Fermi contours which has important implications for spin excitations at surfaces. @FootnoteText@ @footnote 1@E. Rotenberg, J. W. Chung, and S. D. Kevan, Phys. Rev. Lett. 82 4066 (1999). @footnote 2@S. LaShell, B. A. McDougall, and E. Jensen, Phys. Rev. Lett., 3419 (1996).

11:40am **SS3+EM-WeM11 Resonant Auger Studies of Metallic Systems***,* ***I. Coulthard****, J.W. Freeland, S.P. Frigo, J.F. Moore, W.S. Calaway, M.J. Pellin, M. Mendelsohn,* Argonne National Laboratory*; T.K. Sham, S.J. Naftel,* University of Western Ontario, Canada*; A. Stampfl,* Australian Nuclear Science and Technology Organization

Auger electron emission at photon energies near the asoociated absorption edge which generates the initial core hole is a complex process. Excitation and decay become linked such that the process must be described as a single-step process rather than the classical two step process for Auger emission. This results in the production of discrete lines which are resonantly enhanced at the absorption edge, and whose intensity vanishes far below or above the edge. Another result of utilizing resonant photon energies is that the Auger line width may no longer be limited by the intrinsic lifetime resulting in a narrowing of the Auger spectrum.@footnote 1@ Results will be presented for a variety of systems including, Cu, Co, Al, CuNi alloys, and CuAl alloys. Specific attention will be paid to:probing unoccupied densities of states, very high resolution x-ray absorption spectroscopy utilizing auger yields to produce sub-lifetime narrowed x-ray absorption spectra, and the use of the technique for non-homogeneous sample systems. Work at Argonne is supported by the U.S. Department of Energy, Basic Energy Sciences, under Contract No. W-31-109-Eng-38. @FootnoteText@@footnote 1@T.M. Grehk, W. Drube, R. Treush, and G. Materlik. Phys. Rev. B 57, 6422 (1998).

Thin Films Division

Room 615 - Session TF+MM-WeM

Thin Films in MEMS and MOEMS

Moderator: S. Patton, Air Force Research Laboratory

8:20am **TF+MM-WeM1 Detection of Photons Using Thin Films in Semiconductor MEMS**, ***P.G. Datskos****, S. Rajic,* Oak Ridge National Laboratory*; I. Datskou,* Environmental Engineering Group, Inc.

We report on a new method for detecting photons using the stress caused by photoelectrons emitted from a thin metal film surface in contact with a semiconductor microstructure which forms a Schottky barrier. As photoelectrons diffuse from the metal film into the microstructure they produce an electronic stress. The photon detection results from the measurement of the photo-induced bending of the microstructure. Internal photoemission has been used in the past to detect photons, however, in those cases the detection was accomplished by measuring the current due to photoelectrons and not due to electronic stress. Small changes in position (displacement) of microstructures are routinely measured in atomic force microscopy (AFM) where atomic imaging of surfaces relies on the measurement of small changes (< 10@sup -9@ m) in the bending of microcantilevers. In this work we studied the photon response of Si microcantilevers coated with a thin film of Pt. The Si microcantilevers were 500 nm thick and had a 30 nm layer of Pt. Photons with sufficient energies produce electrons from the platinum-silicon interface which diffuse into the Si and produce an electronic stress. Since the excess charge carriers cause the Si microcantilever to contract in length but not the Pt layer, the bimaterial microcantilever bends. In our present studies we used the optical detection technique to measure the photometric response of Pt-Si microcantilevers as a function of photon energy. The charge carriers responsible for the photo-induced stress in Si, were produced via internal photoemission using a 1550 nm wavelength diode laser.

8:40am **TF+MM-WeM2 Sputtered Coatings for Microfluidic Applications***,* ***D.W. Matson****,* *P.M. Martin, W.D. Bennett, J.W. Johnston, D.C. Stewart, C.C. Bonham,* Pacific Northwest National Laboratory

Magnetron sputter-deposited features and coatings are finding a broad range of uses in microfluidic devices being developed at the Pacific Northwest National Laboratory (PNNL). Such features have routinely been incorporated into multi-layer laminated microfluidic components where specific functionality is required and other methods for producing these features have been deemed unacceptable. Applications include electrochemical sensors, heaters and temperature probes, electrical leads and insulation layers, and chemical modification of surfaces. Small features, such as those required for the production of microsensor electrodes or miniature resistive heaters on microfluidic chips, were patterned using standard lithographic methods or with masks produced by laser micromachining processes. Use of the coating technology and its application in specific microfluidic devices, including a groundwater sensor, a piezoelectrially actuated airflow regulator, and a microchannel flow diagnostic device, will be discussed.

9:00am **TF+MM-WeM3 A Novel Thin-Film Proton Exchange Membrane Fuel Cell for Microscale Energy Conversion***,* ***J.D. Morse****, A.F. Jankowski, J.P. Hayes, R.T. Graff,* Lawrence Livermore National Laboratory

A novel approach for the fabrication and assembly of a proton exchange membrane (PEM) fuel cell system enables effective scaling of the fuel delivery, manifold , and cell stack components for applications in miniature and microscale energy conversion. Electrode materials for PEM fuel cells are developed using sputter deposition techniques. A thin film anode is formed through the deposition of nickel, followed by the deposition of a platinum catalyst layer. A proton conducting membrane electrolyte is formed over the catalyst using spin cast techniques. Finally, a thin film cathode is formed that incorporates a thin platinum layer, followed by a layer of silver. Scaling towards miniaturization is accomplished by utilizing novel micromachining approaches. Manifold channels and a fuel delivery system are formed within the substrate that the cell stack is fabricated on thereby circumventing the need for bulky manifold components that are not directly scalable. Methods to synthesize a base electrode layer to a thin-film PEM fuel cell from the electrolyte and a conductive material are developed using photolithographic patterning and physical vapor deposition. The microstructure and morphology desired for the anode layer should facilitate generation of a maximum current density from the fuel cell. For these purposes, the parameters of the deposition process and post-deposition patterning are developed to optimize porosity in the anode layer. The fuel cell microstructure is examined using scanning electron microscopy and the power ouput generated is characterized through current-voltage measurement. This work was performed under the auspices of the United States Department of Energy by Lawrence Livermore National Laboratory under contract #W-7405-Eng-48.

9:20am **TF+MM-WeM4 Thin Films in MEMS and MOEMS***,* ***W.D. Cowan****,* Air Force Research Laboratory **INVITED**

Micro-Electro-Mechanical Systems (MEMS) and Micro-Optical-Electro-Mechanical Systems (MOEMS) employ batch fabrication processes to construct miniature devices with macroscopic functionality. Surface micromachined MEMS structures are manufactured by the deposition and patterning of thin films. In marked contrast with conventional fabrication processes (and bulk micromachining), the thin film materials used in surface micromachined structures are formed as the device is processed. In general, the material properties of thin films are not controlled during deposition, and are only measured after processing is completed. Characterization methods include wafer curvature measurements and a variety of test structures. None of the thin film characterization techniques currently employed is entirely satisfactory and all methods rely on process repeatability to be useful. The ultimate performance of many MEMS and MOEMS depends directly on the materials properties of the thin films employed. Processing variations induce variations in materials properties that directly impact device performance. For MOEMS, residual material stresses can cause curvature of nominally flat reflecting surfaces that degrades optical performance. Recent work in which MEMS foundry processes were used to fabricate low-cost deformable mirrors (MEM-DMs) for adaptive optics illustrates the impact of residual material stress on system level optical performance. Residual material stress can be exploited in other MEMS devices to produce unique structures. More precise monitoring and control of film stress during deposition remains as a challenge for MEMS and MOEMS.

10:00am **TF+MM-WeM6 Residual Stresses in MEMS Structures***,* ***B.S. Majumdar****,* UES, Inc.*; W.D. Cowan,* Air Force Research Laboratories*; S. Rogers,* AFIT*; N.J. Pagano,* Air Force Research Laboratories

Residual stresses impose major restrictions on the performance of MEMS devices. Although different techniques have been developed to measure such stresses, they suffer from a number of limitations. We have focused our attention on square and circular micro-mirrors that are supported by electrically activated arms. Permanent curvature in such mirrors arise from thermal and process-generated residual stresses, and they seriously impair mirror performance. In this work, the residual stresses were estimated from curvature measurements on different sized beams using an interferometric technique, complemented by rigorous elastic analysis of composite beams. It is notable that typical analyses is based on Stoney's equation, which is not believed to be valid for the thin MEMS structures. The composite beams consisted of different grades of poly-silicon with and without gold coating, and the measurements and analysis showed consistent results for the different beams and mirrors. In an effort to de-couple the thermal and process component of the residual stresses, curvature measurements were made at different temperatures. The results and analysis technique will be presented in detail, and possible methods to reduce the residual stresses will be discussed.

10:40am **TF+MM-WeM8 Investigation and Modeling of Electrical Resistance in Polysilicon Thermal Actuators***,* ***J.T. Butler****, W.D. Cowan,* Air Force Research Laboratory

This paper reports on investigation and modeling of the electrical resistance of micromachined polysilicon thermal actuators. The availability of models compatible with commonly used circuit simulators such as SPICE are extremely useful for design of integrated microsystems which include thermal actuators. The development of a model for thermal actuators necessitated an analysis of the electrical resistance characteristics of the MEMS fabrication process in order to provide an understanding of a key material property. The thermal actuators investigated in this research were fabricated through the DARPA-sponsored Multi-User MEMS Processes (MUMPs). Hence, a TSUPREM model of the MUMPs fabrication process was created to generate polysilicon resistivity parameters which were then fed into the electrothermal SPICE model. Two types of thermally actuated devices were modeled: a lateral thermal actuator and a thermally actuated piston micromirror. The SPICE model exhibits very close agreement with the measured performance of the polysilicon thermal actuators. The MUMPs process used to fabricate the thermal actuators has three structural layers of polysilicon. The resistivity of each of the MUMPs polysilicon layers varies due to differences in fabrication. Moreover, our resistance measurements of test structures and actuators showed that the resistivity of devices formed from the various MUMPs polysilicon layers also varies based on structure linewidth. A TSUPREM fabrication model of the MUMPs process was generated which validated the empirical resistance measurements and the dependence of resistivity on linewidth. The TSUPREM simulation revealed that the diffusion of phosphorus dopant during the anneal cycles in the MUMPs fabrication process were largely responsible for the variations in resistivity due to linewidth. For small (< 10 (m) linewidth structures, the presence or absence of lateral diffusion of dopant through the sidewall can significantly alter the electrical resistance. The resistivity dependence on linewidth is significant for our thermal actuators because they are designed with elements having linewidths varying from 2 (m to greater than 20 (m. The electrothermal SPICE model augmented with the TSUPREM resistivity data accurately predicted the I-V performance of both the lateral thermal actuator and the thermal piston micromirror. The use of SPICE allows simulation of both the MEMS device and control electronics in the same analysis package and enables the designer to gain insight into the expected performance of the microsystem prior to fabrication. On-going work includes investigation of adding thermal mechanical modeling to our simulation.

Vacuum Metallurgy Division
Room 620 - Session VM-WeM
Advanced Surface Treatments and Coatings

Moderator: A. Inspektor, Kennametal Inc.

8:20am **VM-WeM1 Microstructural and Surface Morphological Evolution at the Atomic Scale during the Growth of Polycrystalline TiN: a TEM, XRD, HT-STM, and Modeling Study*, I. Petrov*,** *S. Kodambaka, P. Desjardins, A. Vailionis, V. Petrova, J.E. Greene,* University of Illinois, Urbana*; L. Hultman,* Linköping University, Sweden*; G. Gilmer,* Lucent **INVITED**

TiN is widely used as a diffusion barrier in microelectronics, as a hard wear resistant coating on cutting tools, and as a corrosion and abrasion resistant layer on optical components. Even though its diffusion barrier and elastic properties are known to be extremely anisotropic, little is known regarding the mechanisms and reaction paths leading to the development of preferred orientation in polycrystalline TiN layers deposited by PVD. We have used in-situ temperature-dependent STM measurements during deposition and post-annealing, detailed post-deposition microstructural analyses, and modeling to provide atomic-scale insights into microstructural and surface morphological evolution during TiN film growth. The results show that TiN layers grown at low temperatures (@<=@ 450°C, T@sub s@/T@sub m@ = 0.20) exhibit competitive texture evolution with a columnar 111 "kinetically-limited" texture eventually becoming dominant. The columns are narrow with inter- and intracolumnar porosity and facetted surfaces. Higher growth temperatures or the use of high incident N@super +@@sub 2@/Ti flux ratios (> 5) with low ion energies (20 eV) result in non-competitive growth with the development of a fully dense essentially complete 002 preferred orientation from the initial monolayer. The above microstructural results can be understood qualitatively assuming that the activation energy E@sub s@ for surface diffusion and the Ehrlich barrier E@sub b@ at descending step edges are larger on 111 surfaces than on 002. Using this, together with the assumption that pseudomorphic forces (i.e., local epitaxy) dominate once island orientation is determined locally, the general features observed in the experiments outlined above can be replicated using kinetic Monte Carlo simulations. The in-situ STM observations of the dynamics of island growth and decay also provide important additional insights into the atomic-scale growth of TiN and related transition-metal nitrides.

9:00am **VM-WeM3 High Refractive Index -Textured Cubic Zirconia Formed in Nanolaminate Coatings Using Titania Interruption Layers*, J.D. DeLoach,*** University of Wisconsin, Milwaukee*; C.R. Aita,* University of Wisconsin, Milwaukee, US

Thermodynamic phase evolution of bulk zirconia cooled from the liquidus (2680 @super o@C) is as follows: cubic (2360 @super o@C) to tetragonal (~1075 @super o@C) to monoclinic (STP phase). However, the pseudobinary zirconia-yttria phase diagram shows that the cubic phase is stabilized at room temperature by adding approximately 10 mole % yttria. Therefore, most reports of cubic zirconia formation in coatings of practical thickness involve yttria-doped zirconia. Undoped zirconia single layer film studies report the transformation from cubic to monoclinic zirconia with increasing crystallite size, suggesting that a finite crystal size effect aids in cubic zirconia stabilization. For this reason, zirconia phase control is easier in a multilayer scheme, by the introduction of growth interruption layers. This approach was taken by several investigators who grew cubic zirconia in zirconia/yttria nanolaminates. In these cases, cubic zirconia was formed by heteroepitaxy with either -texture cubic yttria or a -texture interfacial cubic zirconia-yttria alloy. The drawbacks of using yttria for growth interruption layers were: (1) the refractive index of the nanolaminate was considerably lowered by the presence of yttria, and (2) the -texture of cubic zirconia was stabilized by heteroepitaxy, precluding a -texture desirable for certain applications. In this study, a sputter-deposited nanolaminate structure consisting of polycrystalline zirconia-vitreous titania bilayers was used to fabricate high refractive index, undoped cubic zirconia coatings with a strong crystallographic texture. Titania was chosen as the interruption layer material because: (1) its vitreous nature encouraged low surface energy {200} cubic zirconia planes to preferentially orient parallel to the growth interface, resulting in a -texture, and (2) its high refractive index resulted in a nanolaminate with an overall refractive index of 2.23.

9:20am **VM-WeM4 Tribological Performance and Initial Finite Element Modeling of Reactively Sputtered Single and Multi-layer Chromium Nitride Thin Films*, S.L. Rohde*,** *D. Mihut, S. Kirkpatrick,* University of Nebraska, Lincoln

This work examines the tribological properties of CrN and Cr@sub 2@N thin films both as single-layers and in a number of different multilayer structures combining CrN, Cr@sub 2@N and Cr. The overall program goal was to test the feasibility of "building-in" load support, by alternating hard/soft film layers to optimize performance on hard materials, such as hardened tools steels, as well on compliant materials like Al-alloys. The first phase of this program centers on the deposition and evaluation of an array of coating structures on various substrates. Thin films were deposited in a mixed Ar-N@sub 2@ discharge, using a single unbalanced magnetron cathode with a Cr-target operating in a metallic-mode. Three differing substrate materials were coated; 52100 bearing steel, A2 tool steel and 2024-alloy aluminum. The adhesion of the thin film/substrate couples was evaluated using scratch adhesion and Rockwell C indentation testing. Scratch adhesion values were found to range from 2 to 8 kg depending on the hardness of the substrate material; with the lowest values occurring on the most compliant substrates (i.e. 2024 Al). The wear behavior was assessed using pin-on-disk and high frequency Cameron-Plint testing. The pin-on-disk tests were performed without additional lubrication at 40 to 50% humidity using alumina and/or tungsten carbide balls as the pin materials. . The wear was reduced in most cases, with the multi-layered structures performing best on all substrate materials. The lubricated Cameron-Plint tests run on coated 52100 steel substrates favored the Cr@sub 2@N-based films, although the hardness of these multilayers is frequently lower than the corresponding CrN-based structures. While on the A2 tool steel substrates, the hardest thin film structures yielded the best PoD wear performance, 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 film 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. Finite element modeling studies have been initiated to try to understand the behavior of these multilayered coating/substrate combinations under specific loading conditions. While still in it's earliest stages, the ultimate goal of the modeling program will be to facilitate design and optimization of application specific coating structures into the original component design stage. To accomplish this models are being developed for previously tested film structures on various substrates, and 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.

9:40am **VM-WeM5 Protective Coatings for Extreme Environments*, H.W. Holleck,*** Forschungszentrum and Universität Karlsruhe, Germany **INVITED**

Physical Vapor Deposition (PVD) allows multifunctional protective coatings to be achieved for extreme and very complex loading situations. Among various thin-film concepts such as superhard coatings, gradient coatings, composite coatings, superlattice coatings, solid-solution coatings, metastable multifunctional coatings, nanoscale coatings, designed to improve the performance of protective coatings, the nanostructured multilayer films, the nanocrystalline composite films, and the metastable vapor-quenched compound films are able in particular to meet extreme requirements. Knowledge of specific design principles has developed over the past few years, thus adding a scientific design basis to what used to be empirical film development. Properties and functions simultaneously attainable include high levels of hardness, toughness, oxidation and corrosion resistance, abrasion and erosion resistance, as well as low friction and low wear in many applications. Multilayer coatings combining metallic hard materials e.g. TiC and TiN or TiAlN, metallic and covalent hard materials e.g. TiC and C or SiC, as well as combinations of hard and soft materials, e.g. TiN and MoS2 or C, will be discussed. Functional and structural contributions are responsible for the changes in properties produced by different numbers of single layers. Relations similar to those applying to multilayer coatings can be found for nanocrystalline films, with the grain size being the most important parameter besides phase composition. An almost unlimited source of new multifunctional coatings meeting extreme requirements are vapor-quenched multicomponent films combining materials of different hard material groups in a homogeneous film material optimized with respect to composition and structure. Examples to be discussed are TiC,TiN, TiB2, and CrN combined with compounds such as BN,B4C, SiC, and AlN. Thermodynamic and kinetic modeling of the coating system and the deposition process allows the constitution, properties and performance of these coatings to be tailored within broad limits.

10:20am **VM-WeM7 Interface Engineering in a Combined Arc/ UBM Deposition System during Growth of Ti@sub 0.5@Al@sub 0.5@N Films on Steel: Effects of Substrate Ion Etching***, **C. Schönjahn**, L.A. Donohue, D.B. Lewis, W.-D. Münz,* Sheffield Hallam University, UK*; R.D. Twesten, I. Petrov,* University of Illinois, Urbana

In-situ substrate cleaning by ion etching prior to deposition in PVD processes is a key step in achieving good film adhesion, which is essential for all coating applications. Irradiation with metal or gas ions alters substrate surface chemistry, topography and microstructure thus affecting subsequent film growth. This study compares Ti@sub 0.5@Al@sub 0.5@N/ steel interfaces formed after Cr- metal ion bombardment at negative substrate biases, Us, ranging from 600 to 1200 V during a Cr cathodic arc, stabilized with a 0.06 Pa Ar background pressure. Samples pretreated with a 1200 V Ar glow discharge at a pressure of 0.6 Pa were also investigated. Microstructure and microchemistry of the interfaces was studied by XTEM samples using STEM-EDX analysis. Cr ion etching with Us = 1200 V resulted in a net removal of over 100 nm of substrate material with the formation, through implantation and radiation-enhanced diffusion, of a Cr-enriched near-surface region extending to a depth of ~10 nm. As Us was reduced to 600 V, Cr accumulated at the surface as an ~5 nm thick layer. Ar was incorporated at the surface to levels of 4 and 5 at % during Cr arc-etching and Ar glow discharge, respectively. Microstructure of Ti@sub 0.5@Al@sub 0.5@N overlayers was dramatically affected by pre-treatment procedures. Ar sputter cleaned steel surfaces (Us = 1200 V) promote nucleation of randomly oriented grains leading to a competitive column growth with small column size and open boundaries. In contrast, Cr irradiation at the same bias voltage results in local epitaxial growth of Ti@sub 0.5@Al@sub 0.5@N on steel, which is expected to improve film/substrate adhesion. Coatings deposited after Cr treatment with Us = 600V still exhibit small areas of oriented growth but porosity is also present.

10:40am **VM-WeM8 Plasma Treatment of Polycarbonate for Improved Adhesion***, **A. Hofrichter**, P. Bulkin, B. Drévillon,* CNRS Ecole Polytechnique, France

The deposition of silicon alloys for protective and optical coatings on polymers is of increasing interest. The understanding of the plasma polymer interaction is of prime importance here. In this work we report a study of the influence of various plasma-treatments on polycarbonate (PC) in order to clarify the adhesion mechanisms of plasma deposited silica films. Treatments and depositions were carried out in a low pressure (1 mTorr range) integrated distributed 2.45 GHz microwave electron cyclotron resonance reactor, which allows the deposition of dense stoechiometric silica at room temperature. The plasma-polymer interaction is studied by in-situ spectroscopic ellipsometry from near UV to infrared and ex situ Raman spectroscopy and atomic force microscopy. The influence of process parameters, such as power and gas composition is studied. To get better insight into the plasma modification mechanisms thin polymer layers, spincoated onto various substrates were used. This allows a precise determination of the absorption properties and the thickness evolution of the plasma modified surface layer by UV-visible ellipsometry. The absorption in the PC layer was found to increase in the UV and is attributed to the different reaction products of photo-Fries rearrangements. Particular attention was taken to evaluate the contribution of the VUV photons. The chain scission and crosslinking of pure and commercial grade polycarbonate is studied by gel permeation chromatography and correlated to the ellipsometric results. Finally we discuss the influence of the treatement on the silica adhesion, evaluated by microscratch test measurements.

11:00am **VM-WeM9 The Effects of Electron Beam Assistance on the Properties of Ion Beam Deposited CN Thin Films***, **Y.H. Kim**, D.Y. Lee, I.K. Kim, H.K. Baik,* Yonsei University, Korea

For the direct ion beam deposition process, the kinetic energy of ion beam have been considered as a main factor for the determination of the properties of resulting thin films. But we have investigated the effects of electron beam assistance on the properties of thin film during the ion beam deposition process of CN material. For the verification of the charge-enhanced chemical bonding, the properties of carbon nitride thin films deposited with and without electron beam assistance are compared. For the direct ion beam deposition process, negative carbon ion beam and positive nitrogen ion beam was used simultaneously. Total negative beam including negative carbon ion and electron can be emitted from the Cs ion bombardment on the graphite target. The filtering of electrons from the total negative beam by the transverse magnetic field is possible and the pure negative carbon ion beam was deposited with positive nitrogen ion beam for the less charge-enhanced chemical bonding process. The properties of DLC and CN thin films were discussed respectively by comparing the thin film growth with and without electron beam assistance. The properties of thin films were characterized by Raman spectroscopy, AES and XPS.

Vacuum Technology Division
Room 610 - Session VT-WeM
Vacuum Pumping Systems

Moderator: B.R.F. Kendall, Elvac Laboratories

8:20am **VT-WeM1 Affect on Pumping-Speed Measurements Due to Variations of Test Dome Design Based on Monte-Carlo Analysis***, **S.B. Nesterov**, Yu.K. Vassiliev,* Moscow Power Engineering Institute, Russia*; R.C. Longsworth,* IGC-APD Cryogenics, Inc.

Test domes for measuring pumping speed are defined in AVS Standard 4.1, Pneurop Standard PN5ASRCC/5 and the last draft of the new AVS Standard for Cryopumps. These test domes are similar. They try to provide a measure of the speed of a pump as if it is mounted in the center of a large, flat plate in a large chamber. In this case, the flow distribution is diffuse while in the test dome the flow pattern has a stronger axial component. The location of the pressure gauge is intended to compensate for the different flow pattern. Certain parameters in the design of the test domes are not rigidly specified -- including the shape for the top of the dome, the diameter of the gas feed tube for the single-dome method or the orifice for the two-gauge method. A Monte-Carlo Analysis has been carried out to analyze the differences in speed which will then be measured for different configurations for the top of the test dome, different gas feed-tube diameters and different diameters of the hole in the aperature plate. Variations in the range of 2% to 3% are calcualted. In addition, a comparison of pumping speed for an APD Cryogenics Marathon 8 Cryopump mounted in a test dome vs. being mounted on a flat plate in a large chamber is presented in order to illustrate the potential affect of the cryopump geometry.

8:40am **VT-WeM2 A Highly Simplified and Reliable Means of Regenerating Closed-Loop Gaseous Helium Cryopumps***, D.W. Crone, J. Brady, M.O. Foreman,* Ebara Technologies Inc.*; **K.M. Welch**,* Consultant

A unique means of regenerating closed-loop, gaseous helium refrigerator cryopumps is reported. If one reverses the rotation of the expander motor of a Gifford-McMahon refrigerator, the thermodynamic cycle is reversed and heat rather than refrigeration is produced at the expander cooling stations. The heat input stemming from reversing the thermodynamic cycle may be used in a controlled manner to achieve a simple, safe and effective regeneration cycle of the cryopump. This reverse cycle regeneration process, and its effectiveness and reliability will be described.

9:00am **VT-WeM3 Review of Pumping by Thermal Molecular Pressure***, **J.P. Hobson**,* National Vacuum Technologies Inc., Canada*; D.B. Salzman,* Polychip Inc. **INVITED**

Pumping energy is supplied by temperature changes only. A general feature of such pumps is that the upper pressure limit is reached when the mean free path becomes small relative to the physical dimensions of the pump in the region of the temperature transition. Thus the upper pressure limit of these pumps has been determined by the microfabrication technology of the day; they have operated at relatively low pressures, with low throughputs, and have not become main-line pumps. In recent years, however, MEMS (Micro-Electronic-Mechanical Systems) has introduced a whole new level of miniaturization to devices in general, including vacuum devices, and hence has raised the upper pressure limits, and thus the throughputs, of thermal molecular pumps to near atmospheric levels.@footnote 1@ The purpose of this paper is to review various physical manifestations of pumps using thermal molecular pressure, which have been realized over the years. Emphasis is placed on pumps which have actually been constructed and tested. The general pumping phenomenon has had various names: the Knudsen compressor, thermal transpiration, thermal creep, thermodynamic, thermomolecular, thermal molecular, and accommodation pumping. This multiplicity of names can cause some confusion and it is one of the objectives of this review to simplify this situation. We have chosen to title the paper "Review of

Pumping by Thermal Molecular Pressure", following the terminology used by Knudsen.@footnote 2@ It is found that, broadly speaking, these pumps divide into two classes: (a) those using no explicit surface treatment; and (b) those using specially prepared surfaces. It is further found that pumps in class (a) have both an upper and lower bound in pressure, while pumps in class (b) have only an upper bound in pressure. A Table is assembled comparing experimental results of pumps which have actually been built and tested. However, scaling rules for multiple stage pumps, based on results obtained for single stage pumps are presented. Despite their diversity thermal molecular pumps all have the compelling advantage that there are no moving parts, nor any fluids, in the vacuum. @FootnoteText@ @footnote 1@ S.E.Vargo, E.P.Muntz, G.R.Shifflet, and W.C.Tang, J. Vac. Technol. A, (in press). Paper presented at the 45th International Symposium of the American Vacuum Society, Baltimore, 1998. @footnote 2@ M.Knudsen, "The Kinetic Theory of Gases", Methuen’s Monographs on Physical Subjects, John Wiley and Sons Inc., New York, 1934.

9:40am **VT-WeM5 Inner Pressure Measurement of Turbo Molecular Pump*, H.-P. Cheng,*** *R.-Y. Jou, J.-C. Lin, F.-Z. Chen, Y.-W. Chang,* Precision Instrument Development Center, National Science Council, Taiwan, ROC

In the past decades, a lot of papers have been published to deal with the pumping mechanism of turbo molecular pump. These articles contain theoretical and experimental investigations. But there are only few of articles contain the experimental data can supply to the comparison with the theoretical models. Most of previous experimental works devoted on the measurement of pumping speed and compression ratio of one stage turbo blade structure or one whole pump. The foregoing review shows that no related work has been published to measure the pressure variation of inner pump from inlet to outlet ports. In this study, the inner pressure measurement of a new type turbo molecular pump is investigated. The pump is developed by the cooperation of Kashiyama Industries Ltd. and Precision Instrument Development Center with a desire to replace the mechanical booster pump. The experimental measurement is followed by the Japan standard JVIS-005. The flow meter method is adopted here. In order to measure the pressure variation from pump inlet to outlet, there are 9 holes with 6.5-mm inner diameter are drilled through the casing of pump along the axial direction. The distances of 9 holes from the plane of inlet port are 49.5, 79.5, 107, 127, 147, 167, 187, 207, and 227 mm. The metal gasket face seal fittings with inner diameter 3-mm are welded into the holes by TIG-Tungsten inert gas welding method. The vacuum gauges with the range of 1.E-4 to 10 torr are linked with metal gasket face seal fittings by the metal bellow tube. Six sets of inlet pressures with 1.E-4, 1.E-3, 1.E-2, 0.1, 0.5 and 1 torr are measured. The pressure variations along the axial direction are plotted versus normalized axial distance. The pressure tendency related to rotor shaped is discussed. Tendency of pressure variation of measurement and prediction is compared.

10:00am **VT-WeM6 Measurement of Axial Pressure Distribution on a Rotor of a Helical Grooved Molecular Drag Pump*, T. Sawada,*** *W. Sugiyama,* Akita University, Japan*; K. Takano,* Mitsui Zosen Ltd., Japan

The theory in regard to the pumping performance of a helical grooved molecular drag pump proposed by the authors has been employed successfully as a design and evaluation tool. However, some researchers presented results different from the authors' using direct simulation Monte Carlo method. Their method included the inlet effect and the secondary flow in grooves either of which was neglected in the authors' theory. This study was planned to examine the validity of the authors' theory precisely. A helical grooved cylindrical rotor was located concentrically in a smooth sleeve. In order to obtain the pressure distribution on the rotor, several taps were installed on the sleeve along axial direction. The taps led to one side of a differential pressure gauge via valves and the upstream side of the rotor was connected to the other side of the gauge. The pressure was measured by switching the valves in turn. The measurements show that (a) the pressure in the free molecule flow regime increases exponentially from the inlet to outlet, (b) the pressure increases almost linearly from the inlet to outlet in the slip and viscous flow regime, and (c) the inlet effect becomes remarkable in the turbulent flow regime. The validity of the theory has been proved from the free molecule to viscous flow regimes, but the theory needs modification so as to include the inlet effect in the turbulent flow regime.

10:20am **VT-WeM7 An MHD Plasma Vacuum Pump*, E.S. Ensberg,*** Microwave Plasma Products, Inc.

The demand for increased productivity in high vacuum plasma processing chambers calls for greater vacuum system throughput. Pump manufacturers have responded by refining turbomolecular and drag pump designs to raise speed and operating temperature limits. Plasma pumps, in a modular design with no moving parts, offer an alternative to rotating machinery for transport of large quantities of gas, especially light or inert gases. The concept depends on the Lorentz force j x B to generate a pressure gradient, directed from the inlet to the outlet of each of an array of channels. The transverse magnetic field B is provided by permanent magnets incorporated in the channel array. Microwave electric fields, parallel to B, form the plasma within the channel array. A steady electric field E, between stainless steel electrodes in each channel, drives the transverse current density j, such that j x B is always directed from the inlet to the outlet region of each channel. Measurements of compression ratios and of throughput per channel vs. pressure (in the range 0.001 to 1 Torr) in evolving laboratory models employing these concepts are reported, together with an approach to modelling transport of plasma and neutrals in the channels.

10:40am **VT-WeM8 Stable Sputter Ion Pump Design*, J.B. McGinn,*** FEI Company

Title: Stable Sputter Ion Pump Design Abstract: The cause of unstable leakage currents in diode sputter ion pumps (SIP) was investigated. The discharge current of diode SIP's of various designs was monitored through a testing protocol of alternate gas exposures. Discharge current instabilities were detected after gas exposures. Specific patterns of current instability were found characteristic to the gas exposure sequence and pump design parameters. Post-mortem examination revealed fields of dendritic protrusions on the cathode plates localized upon the highly ion bombarded cathode craters. Dendritic protrusion density was greatest in cathode craters adjacent to either virtual anode cells or standard cylindrical anode cells optimized for maximum current with close anode to cathode spacing. The dendritic protrusions were found to be responsible for field emission based unstable leakage currents. Various high stability diode SIP's were built and characterized. High stability was achieved through the implementation of the optimal combination of anode cell diameter, anode to cathode spacing, operating voltage and magnetic field as was found necessary to minimize the growth rate of dendritic protrusions. An ultra-high stability diode SIP was built and tested incorporating a muffin tin cathode shape in conjunction with the elimination of virtual anode cells. Single Penning cell optimization results are presented. J. B. McGinn FEI Company 7425 NW Evergreen Pkwy Hillsboro OR 97124 jbm(at)feico.com (503) 640-7580.

11:40am **VT-WeM11 Dry Vacuum Pumps for Semiconductor Processes - Guidelines for Primary Pump Selection*, P.A. Lessard,*** Varian, Inc.

Each of the many processes used for the production of ultra-large scale integrated (ULSI) devices or flat panel displays (FPD) has its own chemical and physical requirements. Many require a vacuum environment that may range from slightly below atmospheric to ultrahigh vacuum (UHV). Requirements for system cleanliness often dictate an oil-free pumping system. This paper discusses each of the process classes which require a dry primary vacuum pump - deposition (both physical and chemical), doping and material removal - and offers guidelines for the selection of the proper pump type. There are three classes of pump needed depending on the severity of the process - clean, moderate and harsh - with escalating complexity and cost for pumps made for the harsher environments. In addition to reviewing some of the latest developments in materials and vacuum design, particular attention is paid to operating experience with the very harshest processes - dielectric deposition and metal etch.

Applied Surface Science Division
Room 6A - Session AS-WeA

Oxides and Insulators

Moderator: C. Pantano, Pennsylvania State University

2:00pm **AS-WeA1 The Pleasure and Pain of Working with Insulators***, **D.R. Baer**, S.A. Chambers, G.C. Dunham, M.H. Engelhard, S.A. Joyce, A.S. Lea, T.M. Orlando,* Pacific Northwest National Laboratory **INVITED**

The detailed understanding of the surface properties of insulating materials is considerably less well developed then that for metals and semiconductors. Some of the reasons for this include the difficulty in getting clean well defined surfaces, the fact that many analysis methods use beams that damage the materials and complications in data collection and analysis due to charge buildup on the samples. The good news is that these materials are very interesting, they are technologically and environmentally important and not as many people are examining them as other materials. Even for analysis of "real" materials and solving applied problems, understanding damage processes, having relevant "reference" spectra, and appropriately dealing with charging effects can mean the difference between success or failure. This presentation will describe some of our research interests involving insulating materials along with a selection of the problems (some with solutions) we have encountered. The presentation will give some examples of deliberate and unintentional beam damage, consequences of heating surfaces, creating and observing defects, methods to prepare "good" and "bad" surfaces, handling charging on difficult materials, and consequences of ion depth profiling. Materials to be discussed will include oxidized forms of Ti, Fe, Pb, Al, and Mg. Examples will include uses of AES, XPS, MBE, and SPM. This work is supported by the Division of Geosciences, Office of Science, U. S. Department of Energy and most of the research performed at the W. R. Wiley Environmental Molecular Sciences Laboratory, a national scientific user facility sponsored by the U.S. Department of Energy's Office of Biological and Environmental Research and located at Pacific Northwest National Laboratory.

2:40pm **AS-WeA3 Surface Segregation in NixCo(1-x)O and MnxCo(1-x)O Solid Solutions***, **M.A. Langell**,* University of Nebraska*; M.W. Nydegger,* Pace Analytical Corporation*; F. Gevrey,* Univ. Framche Comte, France*; G. Couderc,* Univ. Lyon, France

Because of the similarity in crystal structure and compatible nature of their cations, many transition metal oxides systems are miscible over a wide range of composition. For these systems, the bulk structure was investigated by powder x-ray diffraction as early as the mid 1940's, and they are generally observed to follow Vegard's law. We have measured the surface composition of two rocksalt monoxide systems, NiO/CoO and MnO/CoO, which form bulk homogeneous solid solutions over the entire range M@subx@Co@sub(1-x)@O (M =Ni or Mn) of 0@<=@x@<=@1. Surface analysis has been performed with Auger and x-ray photoelectron spectroscopy, the latter of which also provides information on the chemical nature of the cations at the surface of the solid solution. Unlike the bulk material, the surface of both systems shows distinct evidence for segregation of one cation at the expense of the other and appears to be related to the formation of a spinel phase. In the case of the NiO/CoO system the spinel composition is NiCo@sub2@O@sub4@, and for the MnO/CoO system the composition agree with the spinel CoMn@sub2@O@sub4@. Information is also obtained on the octahedral and tetrahedral site occupancy of the cations and on their formal oxidation states.

3:00pm **AS-WeA4 Dynamics of CO Adsorption on O-ZnO: a Molecular Beam Study***, Th. Becker, Ch. Boas, **U. Burghaus**, Ch. Woell,* Ruhr-Universität Bochum, Germany

We present measurements of the initial adsorption probability, S@sub 0@, as well as its coverage dependence, S(@THETA@@sub CO@), of CO on oxygen terminated ZnO(0001) surfaces. Two different substrates with significantly different density of defects, as determined by He atom scattering, were investigated. Using a well defined molecular beam of CO seeded in He the He atom reflectivity could be monitored simultaneously with the flux of backscattered CO molecules. These results allow to separately determine the total sticking coefficient averaged over the whole surface (using the King and Wells method) and the sticking coefficient on flat terraces. Measurements were carried out for different impact energies (48 meV < E@sub i@ < 0.74 eV) and surface temperatures (77 K < T@sub s@ < 800 K). The crystallographic structure and chemical composition of the surfaces have been characterized by LEED, He atom scattering, and XPS. The shape of the S(@THETA@@sub CO@,T@sub s@) curves points to a precursor mediated adsorption, since, for medium (100 - 180 K) surface temperatures S(@THETA@@sub CO@) remains approximately constant up to saturation coverage, @THETA@@sub sat@. For low adsorption temperatures (70 - 90 K) a rather unique shape of S(@THETA@@sub CO@) has been observed, namely an increase of S(@THETA@@sub CO@) with @THETA@@sub CO@ followed by an abrupt decrease when approaching @THETA@@sub sat@. S@sub 0@ is essentially independent of T@sub s@ and decreases linearly with E@sub i@, consistent with a precursor-mediated adsorption and a decreasing probability of adsorption into the precursor state, respectively. The results indicate that the presence of defects does affect the CO sticking probability.

3:20pm **AS-WeA5 Compositional Heterogeneity in Cerium-Based Mixed Oxides Observed by XPS***, **G.W. Graham**,* Ford Motor Company, US*; C.L. Roe,* GE Lighting Division*; L.P. Haack, A.M. Straccia,* Ford Motor Company

It is argued that compositional heterogeneity in certain reducible mixed oxides, like Ce@sub1-x@Zr@subx@O@sub2@, can be inferred from a variation in the metals ratio, as measured by XPS, between fully oxidized and partially reduced states of the oxide, provided that the characteristic linear dimension of the heterogeneity is at least as large as the typical electron inelastic mean free path. The argument is supported by experimental results from two examples involving mixed phases, one in which the length scale is 100 nm and the other in which the domains are too small for detection by standard x-ray diffraction.

3:40pm **AS-WeA6 The Formation of Magnesium Oxide Layer using the MgO Precursor Solution and its Secondary Electron Emission***, **J.H. Lee**,* Samsung Advanced Institute of Technology, Korea*; T.W. Jeong,* Myong Ji University, Korea*; S.G. Yu, H.W. Son, S.H. Jin, W. Yi, Y.S. Choi,* Samsung Advanced Institute of Technology, Korea*; D. Jeon,* Myong Ji University, Korea*; J.M. Kim,* Samsung Advanced Institute of Technology, Korea

The thin layer magnesium oxide having a secondary electron emission coefficient (@delta@) value over 5 is obtained by a spin coating of the MgO precursor solution. The solutions are prepared as an aqueous base using magnesium formate and poly vinly alcohol, or as an organic base using magnesium acetate in 1,3-propanediol which is polymerized by magnesium methoxide. Alkali metal ions including Cs ion are doped by dissolving metal formate or acetate salts additionally in the above solutions. The firing condition, 450 C for 2 hours, is determined by the thermogravimetric analysis data of the dried bulk solution. The XRD measurement of the powder from a firing of the bulk solution at this temperature confirms the MgO crystal structure. The MgO films on Si(100) or ITO glass substrates prepared by a spin coating at 4000 rpm for 40 sec followed by firing at 450 C for 2 hours result in the thickness of 300 Å with a good roughness for a @delta@ value over 5. The doping effect of alkali metal ions of the MgO film is discussed on the regards of the secondary electron emission. The surface morphology and composition are characterized by SIMS, AFM, and SEM. This method allows an easy processing approach with a relatively high @delta@ value, as well as a variety of application into many kinds of structural device such as a microchannel plate with high aspect ratio.

4:00pm **AS-WeA7 Reactivity of Formic Acid (HCOOD and DCOOH) at Uranium and UO2 Surfaces***, **M.T. Paffett**, W.L. Manner,* Los Alamos National Laboratory

Interactions of DCOOH and HCOOD with uranium and UO2.0 surfaces have been examined using surface specific techniques of thermal desorption mass spectroscopy (TDMS), x-ray photoelectron spectroscopy (XPS), and static secondary ion mass spectroscopy (SSIMS). Formic acid dissociates on both surfaces below 100 K to yield surface formate in relatively high yield. On the clean uranium surface a wide range of products are observed after annealing to 200 K which include formate, hydroxyl, and C-Hx (C-Dx,), Oads, and Hads(Dads) groups. Adsorbed formate decomposes by 300 K increasing the concentration of the remaining surface products (especially C-Hx (C-Dx) type moieties). The only gaseous species created in high yields from the clean surface upon annealing are H2, HD, and D2. A small amount of water and methane desorb at higher temperatures. Between 100 and 300 K the predominant species on the UO2.0 surface is surface formate and hydroxyl groups. The presence of surface oxygen stabilizes the formate groups to further dissociation in comparison to the clean uranium surface. Hydroxyl groups react between 300 and 350 K to release water from the surface. Adsorbed formate groups decompose between 400 and 500 K to release CO, COH2 (COD2) groups. Carbon was not detected on the surface by XPS after annealing to 500 K indicating that all carbon containing species either desorb in the form of CO-containing products or dissolve into the surface.

4:20pm **AS-WeA8 Characterisation of Ceramics Thin Films Deposited by Plasma Assited CVD**, ***G. Ceccone,*** European Commission Joint Research Centre, Italy; *P. Colpo,* European Commission, Joint Research Centre, Italy; *M. Baker, P.N. Gibson, P. Sauvageot, F. Rossi,* European Commission Joint Research Centre, Italy

The use of ceramics in biomedical applications has received large attention during the last two decades. In particular, ceramics and glasses have important applications as orthopedic and dental implants. However, since most of bioactive ceramics and glasses are relatively brittle they have to be applied as a coating on high-strength material such as titanium. In this paper, we report the possibility to depositing zirconia coatings by using Inductively Coupled Plasma Assisted CVD technique. Deposition have been performed in a cylindrical ICP reactor from tetra (tert-butoxy)-zircon precursor diluted in argon and oxygen. A 13.56 MHz generator was used for sustain the plasma, whilst the substrate negative bias voltage was controlled by an independent RF generator. The coating microstructural characteristics were investigated by SEM/EDX; XRD was used to assess the coating crystal structure, whereas the coating composition and stoichiometry was investigated by AES and XPS. The mechanical properties of the films have been assessed by nanoindentation and scratch tests. Zirconia coatings having a thickness between 1 and 10µm, and with a maximum hardness of 13GPa have been deposited under different plasma conditions. Correlation between the deposition parameters, such as the gas composition, RF biases, and RF power, and coating properties have been investigated. AES measurements indicate that films having a stoichiometric composition can be deposited over a large range of gas composition, whilst the crystalline structure and mechanical properties of the film are strongly dependent on the ion bombardment energy. The possibility of tailoring the coating characteristics by controlling the ion energy, i.e. the substrate negative bias is presented and discussed.

4:40pm **AS-WeA9 XPS and UPS Characterization of Single Crystal NaNO@sub 3@ and NaNO@sub 2@: Influence of Laser Irradiation at 248 nm**, ***C. Bandis,*** *S.C. Langford, J.T. Dickinson,* Washington State University

Inorganic nitrates are susceptible to radiation damage, including laser and x-ray irradiation. The critical role of radiation induced chemistry is studied utilizing monochromatised X-ray photoelectron spectroscopy (XPS) and He II (40.8 eV) ultraviolet photoemission spectroscopy (UPS). Photoelectron emission from single crystal NaNO@sub 3@ and NaNO@sub 2@ cleaved and laser or x-ray irradiated surfaces shows that the observed changes in the spectra due to laser irradiation are similar with those observed due to X-ray exposure. Our observations suggest that in both cases (laser and X-ray irradiation) the NaNO@sub 3@ decomposition is initiated by the pi-pi* transition in the NO@sub 3@@super -@ anion. Direct comparison of our experimental UPS and XPS valence band electron energy distributions with recent calculations of the total density of states shows good agreement between theory and experiment for both NaNO@sub 3@ and NaNO@sub 2@. We also report on the influence of such surface modification on the laser desorption of ions and neutrals from cleaved NaNO@sub 3@ single crystal surfaces. This work was supported by the Department of Energy (DE-FG03-98ER14864) and the National Science Foundation (DMR-9503304).

5:00pm **AS-WeA10 Surface Defects on Amorphous Aluminum Oxide Films as Corrosion Initiation Sites**, ***K.R. Zavadil,*** *J.C. Barbour, K.-A. Son,* Sandia National Laboratories

The surface activity of chloride ions is viewed as one parameter responsible for corrosion initiation and subsequent breakdown of native aluminum oxide films on aluminum surfaces. One approach to understanding the role of chloride, as well as other corrosion initiators and inhibitors, is to study the surface of tailored oxides that mimic the properties of naturally occurring passive oxides on aluminum. We generate amorphous oxides ranging from tens to hundreds of angstroms thick by exposing electron beam deposited Al films to an O@sub2@ electron cyclotron resonance (ECR) plasma. Surfaces defects in the form of oxygen vacancies are generated at low energy doses of both electron (electron stimulated desorption) and ions (preferential O sputtering). A comparison is made between the activity of vapor phase and solution phase H@sub2@O and Cl at the defective oxide surface by conducting vacuum and solution experiments with a contiguous electrochemical cell. Irradiation and hydration effects are tracked using a combination of Auger electron and x-ray photoelectron spectroscopies as well as temperature programmed desorption. We show that vacancies are active toward vapor phase Cl sorption resulting in surface Cl concentrations of 10@super13@ to 10@super14@ atoms×cm@super-2@. Cl is desorbed from these vacancies at temperatures below 570 K and is displaced by H@sub2@O vapor at room temperature. Defective surfaces show a greater susceptibility to corrosion as measured by a lowering in the pitting potential in 50 mM NaCl solutions. The role of the vacancies in solution appears to be an increase in surface charge resulting in enhanced Cl@super-@ sorption. We find measurable increases in surface oxygen for defective, hydrated alumina surfaces consistent with a surface charge increase. @FootnoteText@ Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the U.S. Department of Energy under contract DE-AC04-94AL85000.

Biomaterial Interfaces Group
Room 613/614 - Session BI-WeA
Biology at the Nanoscale

Moderator: H.G. Craighead, Cornell University

2:00pm **BI-WeA1 Forces and Mechanisms of Self-Assembly: Non-Equilibrium and Transient Effects**, ***J.N. Israelachvili,*** University of California, Santa Barbara, US **INVITED**

Recent experimental and theoretical work has provided new insights into the intermolecular forces and mechanisms involved in the self-assembly of biological structures such as protein complexes, vesicle aggregates and structured biological materials. It appears that many biological structures can only be formed sequentially in space and time, whereby different interactions and processes occur in different regions of space and at different times. The final structure or 'state' is therefore not the thermodynamically equilibrium state, but a 'transient' structure that nevertheless performs its allotted function at optimum efficiency - be it the opening of an adhesion site or conduction pore (with a lifetime of microseconds or milliseconds), a site-specific binding protein (with a lifetime of milliseconds or seconds), a drug-delivery carrier (with a lifetime of days), or a biomaterial with a lifetime of years. Examples will be given to illustrate the generality of such systems, and the implications of non-equilibrium and transient effects to self-assembly in vivo and in vitro will be discussed.

2:40pm **BI-WeA3 Pulling Protein Networks in 2D**, ***G. Baneyx,*** *V. Vogel,* University of Washington

Fibronectin (Fn), an adhesion protein with multiple recognition sites, mediates cell attachment to synthetic and biological surfaces. In solution, Fn exists in a globular state where most of its recognition sites are buried in the protein core. Surface adsorption induces conformational changes in the protein that expose many of these sites. Furthermore, Fn assembles into detergent insoluble fibers on the surface of cells, and these matrices are considered to be the main functional form of the protein. The cell-mediated assembly of Fn into fibrillar matrices is a complex, multistep process that is still incompletely understood. This is due to the chemical complexity of the extracellular matrix, as well as a lack of experimental control over the molecular interactions and dynamic events. We will discuss how Fn fibril assembly into extended two-dimensional networks can be induced by adsorbing Fn from a physiological buffer solution to a dipalmitoylphosphatidylcholine (DPPC) monolayer. A sequential model for the assembly pathway is proposed. Striking similarities are found between the properties of these Fn fibrils assembled underneath DPPC monolayers and those found on cellular surfaces, as well as between the respective sequential assembly pathways. Spontaneous Fn fibril assembly underneath DPPC monolayers can now serve as a well controlled model system to study how different parameters such as the deletion of key Fn sequences, as well as alteration of solution conditions and the presence of other proteins, affect the molecular assembly pathway.

3:00pm **BI-WeA4 Separation of Long DNA in a Microfabricated Channel with Submicron Constrictions**, ***J. Han,*** *H.G. Craighead,* Cornell University

Microfabricated fluid channels with submicron constrictions were used to separate long DNA molecules according to their sizes. The channels were fabricated on Si substrate by photolithography and reactive ion etching techniques, followed by an anodic bonding to make a sealed channel. These channels have alternating thick and thin regions, which allows long DNA molecules to relax during the electrophoretic motion.@footnote 1@ Separation was achieved by the difference in the probability for DNA molecules to escape these 'entropic traps'. Many fluorescence-labeled DNA molecules were collected at the first entropic trap, and launched simultaneously to form a band of DNA molecules. After traveling the channel, each DNA species formed a separated band, due to the mobility difference in the channel. The traveling time of the DNA bands through the channel were measured by monitoring the fluorescence intensity at the end of the channel. Several long DNA species (35~160kbps) were separated as bands in this way, typically within 30 minutes, which is significantly lower than pulsed field methods. Several structural parameters, such as the depth or the length of the thin and thick region, were varied to study the effect on the DNA mobility and the length range of molecules that a given device can separate. Once these relevant parameters are characterized, this device could be a fast way to separate DNA molecules and other polymers. @FootnoteText@ @footnote 1@ J. Han and H. G. Craighead, J. Vac. Sci. Tech. A, in publication (1999)

3:20pm **BI-WeA5 Engineered Nanostructures to Control Microtubule Motion Along Kinesin Tracks***, **J.S. Clemmens**, J.R. Dennis, J. Howard, V. Vogel,* University of Washington

Motor proteins such as kinesin have evolved to transport molecules over long distances along microtubules within cells. The objective of this study is to engineer molecular tracks of motor proteins to direct the motion of microtubules on nanoengineered synthetic surfaces. We have demonstrated that kinesin moves microtubules parallel to nanoscale ridges of shear-deposited poly(tetrafluoroethylene) (PTFE) films,@footnote 1@ presumably due to preferential adsorption of kinesin along specific topographical features. Additionally, we have observed that other proteins adsorb similarly to shear-deposited PTFE films. We aim to elucidate the molecular mechanisms of these phenomena in order to delineate design principles for engineering tracks of kinesin. To accomplish this aim, surfaces have been fabricated with well-defined nanoscale pits and grooves and systematically tested for their ability to preferentially adsorb proteins or motors from solution. Once important topographical features are identified, tracks following specified paths can be engineered. This is the first step in making molecular shuttles that can move, load, and unload cargo between user-controlled locations and against concentration gradients. In the future molecular shuttles may form the basis of transporting molecular cargo through synthetic matrices. @FootnoteText@ @footnote 1@Dennis, JR et al. "Molecular shuttles: directed motion of microtubules along kinesin tracks" Nanotechnology, in press. (1999)

3:40pm **BI-WeA6 Force and Compliance Spectroscopy of Single Peptide Molecule***, M.A. Lantz, S.P. Jarvis, **H. Tokumoto**,* JRCAT, Japan*; T. Martynski, T. Kusumi, C. Nakamura, J. Miyake,* NAIR, Japan

An exciting application of AFM to biology is to measure forces required to stretch and unfold individual molecule. This technique looks very promising for studying molecular structure. However, this work has been applied so far to large proteins with complex structures resulting from a variety of bonding mechanisms. This complexity makes the interpretation of the experimental results difficult. Hydrogen bonding plays a major role in the formation of the secondary and tertiary structures of polypeptides from which proteins are composed. Even though, the detailed energy landscapes involved in the formation of these structures are not well understood. Here we demonstrate a new experimental technique for performing single molecule AFM force spectroscopy on significantly smaller molecules than those previously reported. We have used this technique to study the mechanical properties of the synthetic peptide cystein3-lysine30-cystein, which we designed specifically to study hydrogen bonding. Under the experimental conditions used, the peptide adopts the a-helix structure as a result of hydrogen bonding within the molecule. Force-displacement experiments were used to measure the force (approximately 200 pN) required to stretch single peptides from the helical state into a linear chain and the measured force versus peptide elongation was used to calculate the work done in breaking the hydrogen bonds. The average experimental value of the hydrogen bond energy (20.2 kJ/mol) is in good agreement with reported theoretical calculations. In addition, we directly measured the stiffness of the molecule during elongation and found to vary from approximately 0.005 to 0.012 N/m.

4:00pm **BI-WeA7 Single Molecule Force Spectroscopy by AFM, Nanomechanics Meets Molecular Biology***, K. Tolksdorf, M. Grandbois, M. Rief, H. Clausen-Schaumann, **H.E. Gaub**,* Ludwig-Maximilians-Universität München, Germany **INVITED**

Recent developments in AFM-instrumentation allow the manipulation of single molecules and measurements of intermolecular as well as intramolecular forces. We took advantage of the high spatial resolution of the AFM and developed mechanical experiments with single macromolecules. An overview on this novel kind of spectroscopy will be given and applications in the field of polymer and life sciences will be highlighted: receptor ligand interactions were measured in single molecular pairs. Lateral distributions of interaction partners on samples were mapped in a chemical imaging mode. The length distribution of individual grafted polymers at surfaces was imaged. Individual polymers and proteins that were anchored on a gold surface were picked up with the AFM tip and stretched, their viscolelasticity and yield strength was measured. Proteins were reversibly unfolded and the conformation forces were determined at the level of single secondary structure elements. DNA double strands were stretched and unzipped. A model was developed based on elastically coupled two-level systems that allows the description of basic features of the experimental results. @FootnoteText@ Rief, M.; Oesterhelt, F.; Heymann, B.; Gaub, H. E.Science 1997, 275, 1295-1298. Rief, M.; Gautel, M.; Oesterhelt, F.; Fernandez, J. M.; Gaub, H. E. Science 1997, 276, 1109-1112. M. Rief, H. Clausen-Schaumann , H.E. Gaub, Nature Struct. Biol. (1999), in press M. Grandbois, M. Beyer, M. Rief, H. Clausen-Schaumann ,H.E. Gaub, (1999),Science in press

4:40pm **BI-WeA9 Characterization of Antibody-Antigen Interaction Forces With Magnetic Tweezers***, S. Metzger,* Geocenters*; M. Stevens,* Naval Research Laboratory*; G. Sagvolden,* University of Oslo, Norway*; C. Yanavich,* Nova Research*; M. Natesan,* GeoCenters*; **G.U. Lee**,* Naval Research Laboratory

Living systems have developed the capacity to use molecular interactions to control structure and function. In order to understand the molecular mechanism of these interactions, the force between and within individual molecules has been directly measured using microscopic techniques such as AFM and optical tweezers. We describe a technique for directly measuring intermolecular interactions using magnetic force. This technique allows intermolecular forces to be studied over an extended range of force (10@super-15@ to 10@super-15@ Newton) and time (1 ms to 10 sec). We will demonstrate the principles of this technique by measuring the force and time required to rupture antibody-antigen bonds.

5:00pm **BI-WeA10 Probing the Nano-environments of Peptides on Solid Surfaces by Advanced Secondary Ion Mass Spectrometry***, **T. Schenkel**,* Lawrence Livermore National Laboratory*; K.J. Wu,* Charles Evans & Associates*; A.V. Barnes, M.W. Newman, J.W. McDonald, A.V. Hamza,* Lawrence Livermore National Laboratory

The interaction and bonding of peptides and proteins in the solid phase and on solid surfaces is of central importance in biotechnological research. Embedding of analyte molecules in special matrix solutions (such as 2,5 dihydroxybenzoic acid) has been shown to produce enormous increases in yields of intact molecules both for laser and single charged ion induced ablation. The mechanisms responsible for this enhancement are however not well understood. Both the binding of matrix and analyte molecules in the solid and collisional ion formation processes have been suggested to play important roles. We have investigated the effect of sodium and potassium impurities on secondary ion emission from gramicidin S by time-of-flight secondary ion mass spectrometry (TOF-SIMS) with highly charged projectiles.@footnote 1@ Highly charged ions like Xe@super44+@ or Au@super69+@ increase secondary ion yields by over two orders of magnitude as compared to singly charged ions. Each highly charged projectile emits secondaries from an area of only about 10 nm^2. Analysis of coincidences among secondary ions detected following the impact of a single projectiles allows for the characterization of the nano-environment of e. g. a peptide molecule in a matrix solution. For the gramicidin S, we found that emission of Na@super+@ and K@super+@ ions was strongly correlated with emission of sodium and potassium adduct ions, [M+Na]@super+@, [M+K]@super+@. This correlation indicates the nestling of sodium impurities around peptide molecules. In our presentation we will discuss the potential of coincidence analysis in TOF-SIMS for the probing of nano-environments on surfaces of biomaterials. @FootnoteText@@footnote 1@A. V. Hamza et al., J. Vac. Sc. Technol. A 17, 303 (1999) Acknowledgement: This work was performed under the auspices of the U. S. Department of Energy by Lawrence Livermore National Laboratory under contract No. W-7405-ENG-48.

Electronic Materials and Processing Division
Room 608 - Session EM-WeA

Novel Materials and Devices for Computation and Communication

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

2:00pm **EM-WeA1 Materials and Devices for Optical Communication*, K.J. Vahala,*** California Institute of Technology **INVITED**

The performance requirements of commercial lightwave communication systems have systematically exceeded expectations for over a decade. Driven by explosive Internet growth, current commercial trunk-line systems are approaching 1 Terabit/sec of aggregate bandwidth on a single optical fiber and use as many as 80 channels (wavelengths). Optical switching, channel add/drop, wavelength conversion, and other functions are needed in these systems and there is a premium on functions that can be all-optical and preferably fiber based. This talk will over view some of the materials and devices that are now finding use in telecom systems. It will also suggest some performance issues in these systems that are material-related.

2:40pm **EM-WeA3 Nano-Crystal and Quantum-Dot Memories: Implications Small Dimensions, Quantum Confinement and Interface States*, S. Tiwari,*** Cornell University*; A. Kumar, J.J. Welser,* IBM T.J. Watson Research Center **INVITED**

For field-effect devices, one of the most significant effects of scaling of critical dimensions to the 1--10~nm range is a reduction in collective effects whose reproducibility has been so profitably applied over the last many decades. Examples of such collective phenomena are the number of electrons flowing through the channel, the number of electrons transferred during a CMOS switching event, and the number of dopants used to control the threshold voltage. A larger number of electrons flowing in the channel leads to smaller fluctuations in the current, a larger number of electrons transferred during switching leads to smaller fluctuations in the switching voltage levels, and a larger number of dopants leads to smaller fluctuations in the threshold voltage. The scaling of device dimensions has been driven by higher function and lower cost gained from an increase of device density and performance, a lowering of power density, and mixing of logic and memory technologies. Logic and memory have to co-exist at such small dimensions, and the various forms of memory have to be capable of providing a range of performance from high speed to low power and non-volatility. Nano-crystal and Quantum-Dot memories, examples of flash memories, are small dimension structures that utilize quantum-dot(s) between the gate and the channel of a field-effect transistor to store electron(s), which screen the mobile charge in the channel and thus induce a change in the threshold-voltage or conductivity. These quantum-dots are transmissively coupled to the channel and isolated from the gate. Their reduced dimension and confinement brings forth two important features that are absent in the conventional silicon field-effect transistors: a reduced density of states, restricting the states available for electrons and holes to tunnel, and the Coulomb blockade effect, arising from a larger electrostatic energy associated with placing a charged particle onto a smaller capacitance.

3:20pm **EM-WeA5 Fabrication and Manipulation of Silicon Nanocrystals for Non-Volatile Memory Applications@footnote 1@*, L.D. Bell,*** Jet Propulsion Laboratory, California Institute of Technology*; E.A. Boer, D.H. Santamore, H.A. Atwater, K.J. Vahala, M.L. Ostraat, R.C. Flagan,* California Institute of Technology **INVITED**

Silicon-based devices continue to decrease in size, and fast, low-power devices sensitive to small numbers of electrons are now feasible. MOS structures with large arrays of Si nanocrystals can form the basis for a floating gate memory that is extremely fast, reliable and non-volatile, and in which charge stored may be as little as one electron per nanocrystal. To date, these devices have exhibited a distribution of charge transit times during writing of nanocrystal ensembles, which limits speed and array uniformity. This could be related to nanocrystal interface states, a dispersion in oxide thicknesses, or nanocrystal size variations. To address these limitations, we have developed an aerosol vapor synthesis/deposition technique for Si nanocrystals with active size classification, enabling narrow distributions of nanocrystal size. One goal of these experiments was to use atomic force microscopy (AFM) to perform nanocrystal manipulation and charging on a single-particle basis. Si nanocrystal structures (such as lines and arrows) have been formed by contact mode AFM and subsequently imaged in non-contact mode without additional particle motion. Single nanocrystal charging by a conducting AFM tip has been observed, detected as an apparent height change due to electrostatic force followed by a slow relaxation as the charge dissipates. To investigate the charge trapping characteristics of nanocrystals in device structures, we have made samples of Si nanocrystals embedded in thermally grown SiO@sub 2@ films by ion implantation of Si, followed by annealing at 1100°C. A conducting AFM tip has been used to inject charge into these samples and to observe the charge dissipation as a function of time. The relative contributions of surface defects, bulk irradiation damage and nanocrystals to the resultant trapped charge have been studied and have been shown to be dependent on processing parameters. @FootnoteText@ @footnote 1@Research supported by JPL DRDF and NASA.

4:00pm **EM-WeA7 Architectonics of Defect-Tolerant Molecular Circuitry*, R.S. Williams,*** Hewlett-Packard Labs **INVITED**

Economic and physics considerations indicate that the exponential scaling of CMOS will saturate in a decade. However, the power efficiency of present electronics technology is at least a billion times smaller than the non-reversible thermodynamic limit.@footnote 1@ Thus, there is a huge incentive to invent new devices with nanometer dimensions. In addition, vast quantities of these devices must be manufactured and interconnected inexpensively. Two lines of complementary research are necessary for future nanoelectronics: the development of quantum-state switches and the design of circuit elements that can be assembled into complex systems via chemical processes. A recent proposal for the construction of molecular-electronic computers involves the explicit incorporation of defect tolerance, which is the capability to operate perfectly even in the presence of manufacturing mistakes, into the architecture of the circuit.@footnote 2@ An example of such a defect-tolerant computer was built and tested at Hewlett-Packard Laboratories with standard Si technology. The Teramac experimental supercomputer replaced logic with memory whenever possible and relied on sophisticated computer algorithms to identify and route around defects. This architecture is currently being explored as the basis for molecular-electronic memory, logic, signal routing and multiplexing/demultiplexing in a joint research project involving HP Labs (the Quantum Structures Research Initiative), UCLA (the research groups of Profs. J. R. Heath, F. Stoddart and V. Roychowdhury) and UC Berkeley (Prof. Paul McEuen). Experimental results on prototype devices and circuits will be presented and discussed. @FootnoteText@ @footnote 1@ R. P. Feynman, Feynman Lectures on Computation, edited by A. J. G. Hey and R. W. Allen (Addison-Wesley, 1996). @footnote 2@ J. R. Heath, P. J. Kuekes, G. S. Snider and R. S. Williams, "A Defect-Tolerant Computer Architecture: Opportunities for Nanotechnology," Science 280 (1998) 1716.

4:40pm **EM-WeA9 Carbon Nanotubes - a New Class of 1D Conductors*, P.L. McEuen,*** University of California, Berkeley and LBNL **INVITED**

Carbon nanotubes are single graphene sheets rolled into nanometer diameter cylinders. They are a new class of one-dimensional conductors that can be either metallic or semiconducting, depending upon their structural details. In this talk, I will discuss experiments by our group to probe the electrical properties of these fascinating systems. Wires are attached to individual tubes and a nearby gate is used to control the charge per unit length of the tube. If the tube is semiconducting, the resulting device operates as the world's smallest transistor. For a metallic tube, behavior characteristic of a correlated electron state known as a Luttinger liquid is found. Short tubes act like one-dimensional boxes for electrons whose quantized energy levels and spin states can be probed. Crossed metal and semiconducting tubes act as ultra-small Schottky diodes. As these experiments show, nanotubes offer an unprecedented opportunity to explore the physics and technology of the one-dimensional electron gas.

Magnetic Interfaces and Nanostructures Technical Group
Room 618/619 - Session MI-WeA

Giant Magnetoresistance

Moderator: B.A. Everitt, Seagate Technology

2:00pm **MI-WeA1 Hot Electron Attenuation Lengths in Magnetic Multilayers*, R. Lu,*** *K.L. Kavanagh,* University of California, San Diego*; C.J. Powell, P.J. Chen, F.G. Serpa, W.F. Egelhoff, Jr.,* National Institute of Standards and Technology

We are using ballistic electron emission microscopy (BEEM) to measure electron transport across magnetic metal multilayers. Room temperature measurements in air have been carried out on Au/M/Si(100) or Au/M/Au/Si(100) diodes, sputter deposited at 175 or 300K, where M is Co, Fe, Ni, or NiFe(81:19). STM images of the 5nm thick Au surfaces show 10-20nm diameter crystallites, with a typical roughness of 3-6nm, depending on the deposition temperature. Corresponding BEEM images show grain dependent BEEM currents, with uniform contrast across each grain, independent of surface morphology, presumeably a function of the Au or magnetic-metal grain orientation. Averaged BEEM spectra for the Au/M/Si diodes, as a function of magnetic metal thickness (0 - 2nm) show decreasing (Ni or NiFe) or increasing (Co and Fe) BEEM thresholds with increasing metal thickness, indicative of changing magnetic metal/semiconductor interface coverage and/or reactions. Plots of log BEEM current versus M thickness are linear giving hot electron (1-1.5eV) attenuation lengths for Co, Fe, NiFe, and Ni of 2, 5, 8 and 13±2Å, respectively. Magnetic metal sandwich diodes, (Au/M/Au/Si) show comparable attenuation lengths but with smaller BEEM currents, likely the result of greater interface scattering. We are in the process of carrying out BEEM magnetotransport measurements on GMR layers and will report these results at the meeting.

2:20pm **MI-WeA2 Exchange Bias in Fe/Cr Double Superlattices*, J.S. Jiang,*** *G.P. Felcher, A. Inomata, R. Goyette, C. Nelson, S.D. Bader,* Argonne National Laboratory

The exchange bias effect is a magnetic pinning phenomenon at the interface between a ferromagnet (F) and an antiferromagnet (AF). It is characterized by a field-offset, or "biased", hysteresis loop. Research on the exchange bias effect has been limited by difficulties in identifying the interfacial magnetic structure and in assessing the role of interfacial roughness. The strength of exchange bias typically observed experimentally is more than an order of magnitude smaller than that predicted by theory. We demonstrate the exchange-bias effect in sputter-deposited epitaxial Fe/Cr "double superlattice" structures that consist of ferromagnetically and antiferromagnetically coupled Fe/Cr superlattices. The AF/F interface in our novel double superlattices is coherent compared to conventional exchange bias systems consisting of dissimilar AF and F phases. The double superlattices offer flexibility in configuration and tunablity of the magnetic coupling and anisotropy. Magnetization results show that AF/F exchange coupling affects the nucleation of reverse magnetic domains, and that the magnitude of the exchange bias field is given directly by the classic formula for collinear spin structures. The collinear spin distribution is confirmed by polarized neutron reflectivity. Work supported by US-DOE BES-MS Contract No. W-31-109-ENG-38.

2:40pm **MI-WeA3 Surface Diffusion Mechanism for the Exchange Coupling between a Ferromagnetic Layer and an Antiferromagnetic Layer*, C. Hou*[1]*,*** *K. Zhang, T. Zhao, H. Fujiwara,* The University of Alabama

It is the surface net spin that is considered to be responsible for the exchange coupling between a ferromagnetic (F) layer and an antiferromagnetic (AF) layer. For an AF surface with roughness, statistics shows that an AF grain with a total number of spins n = n@super +@ + n@super -@, has an average net number of spins pointing in one direction of n@sub net@ = absolute value of (n@super +@ - n@super -@) = n@super 1/2@ with n@super +@ and n@super -@ denoting the number of spins in "+" and "-" directions within one AF grain, respectively. For an AF layer with total grains N = N@super +@ + N@super -@, it is expected N@super +@ /N@super -@ = 1 as deposited without the F layer, where N@super +@ and N@super -@ denote the number of grains with net spin in the "+" and "-" directions, respectively. Therefore the surface spins of all the AF grains still cancel each other. When a F layer is deposited on top of the AF layer under a field in "+" direction, the balance of N@super +@ and N@super -@ is broken, resulting in N@super +@ / N@super -@ > 1. Thus, the overall net moments are obtained without changing n@sub net@ of each grain. It is generally accepted that this is the cause of the exchange coupling. A NiFe/FeMn/NiFe sample shows reasonable amount of exchange bias field H@sub eb@ and coercivity H@sub c@ for both of the NiFe layers as deposited in a field. With post annealing with a field in the pinned direction, it is found that both H@sub eb@ and H@sub c@ of the two NiFe layers are increased. The results can't be explained by the increase of only the ratio N@super +@ /N@super -@. It is concluded that it is the increase of the individual n@sub net@ that causs the above phenomenon. The increase of n@sub net@ is thought to occur through surface spin diffusions.

3:00pm **MI-WeA4 Magnetic Stability of Exchange Coupled Magnetic Systems*, A. Inomata,*** *J.S. Jiang, C.-Y. You, J.E. Pearson, S.D. Bader,* Argonne National Laboratory

The growing demand for higher density magnetic recording and the development of magnetoelectronic devices require controllable magnetic properties on the nanometer scale.@footnote 1@ The application of interfacial exchange coupling is attractive for this purpose. The exchange bias effect occurring at the interface between a ferromagnet(F) and an antiferromagnet(AF) has been used for GMR heads in high density magnetic recording, and exchange-spring magnets consisting of exchange coupled hard and soft ferromagnetic phases are candidates for the next generation of permanent magnet materials. We present a comparison of the magnetic stability in exchange bias and exchange spring systems. The exchange bias system used is the Fe/Cr "double superlattice" structures constructed as [Fe/Cr]@super AF@/Cr/[Fe/Cr]@super F@ with appropriate Cr thickness representing the F and AF.@footnote 2@ And for the exchange spring system we used SmCo/Fe bilayer structures grown epitaxially on different templates to give uniaxial, biaxial and random in-plane anisotropy.@footnote 3@ The switching field and remanent magnetization of both systems were measured by the magneto-optic Kerr effect during repeated reversal of the soft layer magnetization by field cycling. All samples are stable after 10@super +6@ cycles. The effects of the pinning layer and the interfacial spin configuration will be discussed. Work supported by US-DOE BES-MS Contract No. W-31-109-ENG-38. @FootnoteText@ @footnote 1@ S.Gider et al. Science, 281, 797, 1998. @footnote 2@ J.S.Jiang et al. Submitted to Phys.Rev.Lett. @footnote 3@ E.E.Fullerton et al. Phys.Rev.B.58, 12193, 1998.

3:20pm **MI-WeA5 CPP-GMR for Magnetoelectronic Memory*, K. Bussmann,*** *G. Prinz, B. Bass, S.-F. Cheng,* Naval Research Laboratory*; D. Wang, J. Daughton,* Nonvolatile Electronics, Inc. **INVITED**

Current perpendicular-to-plane giant magnetoresistance (CPP-GMR) has been demonstrated to provide enhanced GMR relative to that measured using the current-in-plane (CIP) geometry with similar multilayer architectures. We have been pursuing this advantage in work performed at the Naval Research Laboratory in developing a new non-volatile magnetic memory compatible with existing Si-CMOS technology. The functionality of this approach improves as the device dimension is reduced to sub-micrometer levels. At these dimensions the micromagnetic switching processes are strongly influenced by edge effects and it is important to include these terms, along with intrinsic magnetic materials properties, to obtain stable '0' and '1' configurations. We will show our results on circular disk devices that stabilize the magnetization in right or left-handed helicity. The devices are constructed as magnetic layers separated by non-magnetic spacer layers. Magnetic layers are alternately rendered 'hard' and 'soft' by varying the thickness of the layers as 'thick' or 'thin', respectively. The residual magnetic pole density at the device edge is minimized by the nature of the parallel alignment of the magnetization to the circumference of the disk, an effect driven by the exchange coupling intrinsic to each layer. Parallel and antiparallel helicity orientations of the magnetization are obtained by flowing current through the device, allowing programmability to '0' (parallel) and '1' (antiparallel) states. We show and interpret switching data on devices ranging from 0.25 - 0.6 micrometers in diameter and present an analysis of utility of these structures in CPP-GMR magnetoelectronic memory.

4:00pm **MI-WeA7 High-Speed Dynamics of Submicrometer GMR Devices*, S.E. Russek*,** National Institute of Standards and Technology **INVITED**

Most of the applications of GMR and spin-dependent tunneling devices require them to be very small (line widths of ~300 nm) and very fast (operation frequencies > 1 GHz). The simplest devices typically consist of 4 to 10 layers of magnetic, nonmagnetic, insulator, and conducting materials with thicknesses of 0.6 nm to 10 nm. In this talk I will present high-speed measurements of sub-micrometer spin valves being driven by magnetic field impulses and step excitations with peak widths and ristimes of less than 300 ps. We have observed sub- 300 ps rotations and switching (180 degree rotation) of these devices and free induction decay (damped precessional motion) with characteristic frequencies of 2 - 6 GHz. The response of the devices have been compared to Landau-Lifshitz-Gilbert (LLG) micromagnetic simulations and high-speed measurements of magnetization rotation in sheet films using second-harmonic MOKE. The value of the dynamical parameters of the small devices, such as the damping constant, have been compared to those measured using more traditional methods on larger samples, with a smaller range of motion of the magnetization, and a less complex layer structure. The effect of disorder due to edge roughness, surface roughness, and variable interlayer

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[1] **Falicov Student Award Finalist**

coupling have been studied using LLG simulations and the results have been compared to the dynamical response of real devices to assess the importance of disorder in real systems. Both the damping constant and the degree of disorder are shown to be important in high-speed operation of these devices.

4:40pm **MI-WeA9 RF Diode Sputter Deposition of GMR Multilayers***, **W. Zou**, H.N.G. Wadley,* University of Virginia*; D. Wang, D. Brownell,* Nonvolatile Electronics, Inc.

Radio frequency (RF) diode sputtering has been used for the growth of giant magnetoresistive (GMR) metal multilayers. A systematic series of experiments have been conducted to evaluate the dependence of magnetic properties and magnetoresistance upon growth conditions (i.e. background pressure, input power) for NiFeCo/CoFe/CuAgAu multilayers with different CuAgAu thickness during RF diode sputter deposition using an argon plasma. Atomic force microscopy results have shown that the background pressure and plasma power have large effects upon column width and surface morphology that eventually affect GMR properties. A multiscale modeling study has been used to investigate the origin of these phenomena and to identify the origin of the relationships between the experimental observations and growth conditions. Novel deposition strategies for morphology control have been identified.

5:00pm **MI-WeA10 Effects of UV Illumination on Dry Etch Rates of NiFe-based Magnetic Multilayers***, **H. Cho**, K.P. Lee, K.B. Jung, S.J. Pearton,* University of Florida*; R.J. Shul,* Sandia National Laboratories

Dry etch patterning of magnetic multilayer stacks (eg. NiFeCo/CoFe/Cu/CoFe/NiFeCo) is possible under high density plasma (HDP) conditions using chemistries such as Cl@sub 2@/Ar or CO/NH@sub 3@. The etch mechanism is ion-assisted desorption of metal chloride or metal carbonyl products. Much higher (@>=@ factor of 3) etch rates are achieved with the Cl@sub 2@-based plasma chemistries, but the rates are still limited by desorption of the FeCl@sub x@ or Cu@sub 3@Cl@sub 3@ etch products. Simultaneous UV irradiation of the sample surface during HDP Cl@sub 2@ etching has been found to convert Cu@sub 3@Cl@sub 3@ into more volatile CuCl@sub 2@ and Cu@sub 2@Cl@sub 3@ species, lowering the activation energy for desorption and enhancing the Cu etch rate.@super (1)@ We have studied the effects of UV illumination on the etch rates of NiFe and NiFeCo in Cl@sub 2@/Ar and CO/NH@sub 3@ discharges, and on the etch selectivity of these materials over a variety of different mask materials (SiO@sub 2@, photoresist, photo-definable polymers) as a function of illumination flux, process pressure and HDP source power. For prevention of post etch corrosion it is still necessary to use H@sub 2@O rinsing or in-situ H@sub 2@ or SF@sub 6@ plasma removal of chlorinated etch residues.

The Science of Micro-Electro-Mechanical Systems Topical Conference
Room 620 - Session MM-WeA
Micro-Science and Tribology

Moderator: C. Zorman, Case Western University

2:00pm **MM-WeA1 Micro-Science and Tribology***, **L. Lin,*** The University of Michigan **INVITED**

Microelectromechanical Systems (MEMS) have emerged as an interdisciplinary field in recent years and encompassed a wide range of scientific and engineering areas such as electrical engineering, mechanical engineering, material sciences, physics and chemistry. Tribological issues dealing with adhesion, abrasion, corrosion and erosion are generally encountered in macroscopic machinery and are inevitable problems for micro-science. The technological and economical impacts of tribological issues in MEMS demand fundamental understanding and characterization in material development, design, processing and testing of microstructures. Micro devices that are fabricated by IC (Integrated Circuit) processes represent very different surface features than those macro structures fabricated by conventional mechanical manufacturing processes. It is important to study the micro-science of tribology and investigate the tribological effects in the microscale for optimal design and processing of MEMS. This talk will present several important tribological effects, including surface roughness of the microstructures to the nucleation of micro thermal bubbles, to the mechanical properties and to the optical properties of microstructures. The causes and solutions of the surface force induced sticking failures in MEMS will be discussed. A review of MEMS micromachining processes describing key manufacturing steps is followed by practical engineering examples. Future research directions will be proposed in the conclusion.

2:40pm **MM-WeA3 Deposition, Characterization and Degradation of Vacuum-deposited Fluorinated Alkylsiloxane Films***, **T.M. Mayer**, M.P. de Boer, N.D. Shinn, T.A. Michalske,* Sandia National Laboratories

We deposit monolayer films of fluorinated alkylsiloxanes by a chemical vapor deposition process using C@sub 8@F@sub 13@H@sub 4@SiCl@sub 3@ and H@sub 2@O. Films are formed under well controlled conditions of reactant exposure and temperature, from 25 - 300@super o@ C. Using in-situ ellipsometry and quartz crystal microbalance techniques, we show that film thickness is self limiting at approximately one monolayer due to coverage dependent adsorption of precursors. Adhesion measurements of micromechanical structures coated with these films show typical adhesion energies of ~20 µJ/m@super 2@ at low humidity conditions. Exposure to high humidity environments for long periods results in degradation of the films and stronger adhesion. We postulate that this degradation is related to defects in the films, which are susceptible to hydrolysis by adsorbed water. We examine this postulate by measuring adhesion for varying film coverage, and by examining the morphology of freshly deposited and aged films by atomic force microscopy. Friction measurements correlated to film structure and history are examined as well in micromechanical test devices using structures coated with these films.

3:00pm **MM-WeA4 Vapor-Phase Lubricants: Nanometer-scale Mechanisms and Applications to Sub-micron Machinery***, **M. Abdelmaksoud**, B. Borovsky, J. Krim,* North Carolina State University

The concept of lubricating high temperature bearing surfaces with organic vapors which react with a surface to form a solid lubricating film has existed for at least forty years, with substantial efforts beginning in the 1980's and continuing to the present day. While vapor-phase lubricants have primarily been studied within the context of macroscopic system performance, they may well prove to be of critical importance to tribological performance in sub-micron mechanical systems as well: The vapor phase may ultimately prove to be the most effective, if not only, means to deliver and/or replenish a lubricant on account of the submicron scale of the device itself. In order to investigate the viability of vapor-phase lubrication for MEMS applications, we have studied the molecular scale properties of a number of known or proposed vapor-phase lubricants in controlled environments and well-defined contact geometries.A first study involves Auger Spectroscopy and Quartz Crystal Microweighing investigations of the known lubricant TBPP as it reacts with an iron film surface prepared in ultra-high vacuum conditions. Confirming prior conjecture, we observe that exposure of iron to TBPP vapors results in a rigidly adhering film with a graphitic carbon component which presumably is the lubricating component. With the intent of modelling actual MEMS contacts, we have also constructed a simple nanomechanical system consisting of a Scanning Tunneling Microscope tip dragging on the surface of a Quartz Crystal Microbalance electrode. This system allows us to monitor lubricant performance in realistic sliding conditions. Of the systems which we have observed to date, those films which are associated with the greatest decreases in friction have also been the quickest to wear away due to the rubbing action of the STM/QCM combination. Work is now in progress to study the effect of these vapor-phase lubricants on actual MEMS devices, namely comb motors.

3:20pm **MM-WeA5 Adhesion Performance of Silane Coupling Agents at High Humidity Levels***, **M.P. de Boer**, T.M. Mayer, T.A. Michalske, R.W. Carpick,* Sandia National Laboratories*; R. Maboudian, U. Srinivasan,* University of California, Berkeley

We have measured the effect of humidity on autoadhesion of polycrystalline silicon cantilever beams fabricated by surface micromachining, and coated with silane coupling agents. To make the measurements, we designed and constructed an environmental microprobing station with interferometric capability, and automated the system to enable measurement of beam deflections in-situ. We quantified adhesion by applying a fracture mechanics equilibrium to each adhered beam. For both ODTS (C@sub 18@H@sub 37@SiCl@sub 3@) and FDTS (C@sub 8@F@sub 17@C@sub 2@H@sub 4@SiCl@sub 3@) coatings, the effect of relative humidity (RH) is negligible for RH up to approximately 80%. For ODTS coatings at 99% RH after a 40 hour exposure, adhesion increases only moderately by a factor of two. For FDTS coatings at 90% RH, adhesion increases dramatically by a factor of 100 after seven hours, with further subsequent increases at higher RH values. This is a surprising result, considering that FDTS has a higher contact angle with water than does ODTS, and exhibits lower adhesion at low RH. We believe that defect formation is responsible for the adhesion increase. To support this assertion, we conducted water absorption experiments and obtained atomic force microscopy images revealing agglomerated coupling agent on films exposed to high RH. ODTS is less susceptible to this mechanism than FDTS because of its greater chain length and smaller chain diameter. Our results contrast with experiments on fatty acid monolayers using the surface force apparatus, where uniform swelling of the film is responsible for a monotonic adhesion increase with RH.

3:40pm **MM-WeA6 Adhesion Properties of Gold-on-Gold Microswitch Contacts***, **S. Majumder**, N.E. McGruer, G.G. Adams, P.M. Zavracky, R.H. Morrison,* Northeastern University*; J. Krim,* North Carolina State University

Electrostatically actuated microswitches have been developed at Northeastern University. As part of this effort, gold-on-gold microswitch contacts have been studied on the basis of electrical measurements, surface analysis, and an analytical model of the contacts.@footnote 1@ Measurements show that the turn-off voltage of the switch is often substantially smaller than the turn-on voltage, an effect which is not predicted by an electromechanical model of the actuation mechanism. Also, contact stiction is a dominant mode of eventual switch failure. Motivated by these observations, we extend our study of contacts to include adhesive surface forces at the contact interface. We consider the applicability of the JKR and DMT surface force models.@footnote 2@ to our problem. We examine the validity of these models through various measurements. Under typical operating conditions, the contact force is approximately 40 µN, the spring force which returns the switch to the off position is 150 µN, and the adhesion force (minimum spring force required to turn off the switch) usually ranges from 10-50 µN for a major portion of the switch lifetime (10@super 4@ - 10@super 6@ switching cycles). Failure by stiction is preceded by a gradual increase in the adhesion force. The adhesion force has a strong (inverse) correlation with the contact resistance, and some correlation with the maximum applied contact force during the on-cycle. Other results that are compared with the model include the variation of contact resistance with contact force during loading and unloading, the contact resistance when the switch just turns on and off, and the effect of loading history. @FootnoteText@ @footnote 1@ S. Majumder, N.E. McGruer, P.M. Zavracky, G. G. Adams, R. H. Morrison, J. Krim, Transducers '97, Chicago, IL (1997). @footnote 2@ M. D. Pashley, J. B. Pethica, D. Tabor, Wear, vol. 100, pp. 7-31, 1984. .

4:00pm **MM-WeA7 Environmental Effects on the Tribological Behavior of Silane-Treated Micromachines@footnote 1@***, **M.T. Dugger**, J.A. Ohlhausen, G.A. Poulter,* Sandia National Laboratories

Reproducible performance of silicon surface micromachined devices having contacting surfaces in relative motion requires that contact surfaces maintain uniform friction coefficient over the useful life of the device. High yield fabrication of such structures also requires that the moving surfaces are physically free from other surfaces after the final manufacturing step. Several methods are available to produce hydrophobic surfaces on silica at the conclusion of manufacturing, so that capillary forces do not pull structural elements into contact. These may also favorably affect the friction coefficient and wear characteristics of the treated surfaces. However, these chemical surface terminations may be degraded by wear, and the degradation may be influenced by reactive species present in the gas phase. Polycrystalline silicon test structures have been used to determine the friction coefficient and durability of silane-based surface treatments in controlled environments. Water vapor present in the environment leads to changes in friction coefficient and device failure at fewer operating cycles than when water vapor is absent. Surface analysis and mechanistic aspects of interaction of the silane-treated surface with water vapor will be discussed. @FootnoteText@ @footnote 1@ This work was supported by the United States Department of Energy under contract DE-AC04-94AL85000. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy.

4:20pm **MM-WeA8 Selective Organophosphonate Chemical Sensors Using Self-Assembled Composite Monolayers and Adsorption-Induced Stresses in MEMS Devices***, P.G. Datskos, **H.M. Meyer**,* Oak Ridge National Laboratory*; D. Karst,* Virginia Tech*; M.J. Sepaniak,* 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 opens-up new possibilities for chemical detection. For example, microcantilevers 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. We describe a novel organophosphonate chemical sensor that is based on adsorption-induced stresses in MEMS (micro-electro-mechanical systems) and self-assembled monolayers. The MEMS microcantilever chemical sensor was found to exhibit high sensitivity, reversibility and chemical selectivity. Target molecules adsorbed on the surface of a microcantilever induce a differential surface stress causing changes in both the resonance frequency of the microcantilever and its bending. Measurable changes in the microcantilever bending always occur before any measurable resonance frequency shifts. Monitoring the bending of the microcantilever as molecules adsorb on its surface provides an extremely sensitive means of chemical sensing. In addition, monitoring of resonance frequency changes provides another sensing mechanism similar to the manner SAW and QCM devices operate. The chemical selectivity and reversibility of the present chemical sensor is based on the action of composite self-assembled monolayers. We will report on the response of microcantilevers with composite self-assembled monolayers to DIMP and DMMP. Our results show that such microcantilever chemical sensors exhibit rapid response times and high selectivity to organophosphonate compounds.

4:40pm **MM-WeA9 Nanofabrication and Electrostatic Operation of Single-crystal Silicon Paddle Oscillators***, D.W. Carr, S. Evoy, **L. Sekaric**, A. Olkhovets, J.M. Parpia, H.G. Craighead,* Cornell University

Nanoelectromechanical systems (NEMS) are of interest from both scientific and technological standpoints. Such structures are being considered for use as sensors, force gauges and for various optomechanical and biomedical applications. Small resonant structures also open avenues for mesoscopic studies of the mechanical properties of materials. We have recently reported the fabrication and excitation of single wires with resonant frequencies as high as 380 MHz. Here we report the fabrication and characterization of paddle oscillators with nanometer-scale supporting rods. The devices are electrostatically driven and are detected at room temperature using an optical interferometric technique. The devices show two resonances in the f =1-10 MHz range. We have measured the frequency of both resonances for a series of devices of varying paddle length, d. A fit of data to a f = Kd^b power law reveals experimental power coefficients of b1=-0.5Â±0.1 and b2=-1.6Â±0.15 for the two resonances. These coefficients agree with the values expected for translational and torsional modes of motion, respectively. Our model of the torsional mode suggests that the external drive induces an angular dependent electrostatic torque, resulting in a modulation of the torsional constant. This results in a shift of the resonant frequency under the application of a DC bias. Dependence of this shift on the bias allows us to extract a mechanical torsional constant of tau= 4.21Â±0.04 x 10-12 N.m. This modulation also results in parametric amplification effects that are under investigation. The translational motion shows non-linear behavior at low driving RF amplitudes. A model based on the mechanical stretching of the beams predicts the onset of non-linearity at such amplitudes. Finally, we will discuss the effects of material and surface properties on the dissipative processes in these structures. We are also looking at alternative geometries and potential chemical sensing applications.

5:00pm **MM-WeA10 MEMS-Based Force Detected Nuclear Magnetic Resonance Spectrometer***, **T. George**, W. Tang, A. Chang-Chien, D.W. Elliott,* Jet Propulsion Laboratory*; L. Madsen, G. Leskowitz, D. Weitekamp,* California Institute of Technology

A novel nuclear magnetic resonance (NMR) spectrometer was recently demonstrated. In contrast to conventional NMR spectroscopy, which involves the detection of RF absorption, the force-detection technique works on the principle of using the RF to resonantly invert the magnetization of the sample of interest. The magnetization inversion is carried out at the mechanical resonance frequency of a microfabricated harmonic oscillator consisting of a silicon "diving board" on which a sensor magnet is mounted. The motion of the oscillator in response to the inversion of the sample magnetization is detected using fiber-optic interferometry. A two pronged approach was undertaken to develop the MEMS-based instrument. Microfabrication techniques including deep reactive etching of silicon and micro-electroplating of Fe-Ni alloys are being developed for the 2 mm diameter MEMS instrument. In parallel, a 25 mm diameter, conventionally machined magnet array mounted on a microfabricated silicon "diving board" has been used successfully to demonstrate the proof-of-concept. NMR spectroscopy has been conducted using this device, on millimeter-sized water droplets. Spin-echo experiments have also been undertaken to reduce the linewidth of the

NMR peaks to below <1 Hz. The results of these experiments and the fabrication process will be described in detail. Applications of FDNMR spectroscopy in planetary exploration will also be discussed.

Manufacturing Science and Technology Group
Room 611 - Session MS-WeA

Metrology II

Moderator: A.C. Diebold, Sematech

2:00pm **MS-WeA1 Micrometrology with Scanning Probes***, **H.K. Wickramasinghe,*** IBM T.J. Watson Research Center **INVITED**

Scanning Probe Microscopes (SPM) have become valuable instruments for development and quality control in the semiconductor industry. They provide new capabilities for inspection and metrology of surfaces on a sub-micron scale. The key to their operation is the positioning and scanning of a small tip, or probe, at a minute distance over the surface. The ability to track the position of a surface with an accuracy of the order of a nanometer is advancing the frontiers of micro- or nano-metrology in the semiconductor industry. The standard Atomic Force Microscopes (AFM), using a conical shaped tip, is the most widely used type of SPM for inspection and metrology. This technology essentially measures depth of structures with high precision. Recent technical developments have added the capability to accurately measure width of lines and trenches, using a flared tip and an improved scanning and tracking method for the tip. Other techniques have evolved that measure magnetic properties on the nanometer scale. The talk will review the recent developments of scanning probes with special focus on applications to manufacturing.

2:40pm **MS-WeA3 Chemical Process Sensing using Mass Spectrometry in Multicomponent Reaction Systems***, **Y. Xu**, T. Gougousi, N. Gupta, J.N. Kidder, Jr., G.W. Rubloff,* University of Maryland

A significant number of CVD applications in VLSI manufacturing, such as CVD of W, TiN, SiO@sub 2@, Cu, and more complex high K materials, involve multicomponent reactant mixtures. We have investigated experimentally W CVD processes from H@sub 2@/WF@sub 6@ mixtures in attempts to develop mass spectrometry based thickness and rate metrology approaches. This direction poses a variety of challenges, both fundamental and practical. First, the choice of reactant stoichiometry is dictated by the mechanistics of the application, and typically an overabundance of one reactant is required, so that transport of the other is at least in part rate-limiting. This determines which species is suitable for measurement of reactant depletion for deposition metrology. For example, in SiO@sub 2@ CVD from SiH@sub 4@/N@sub 2@O, the N@sub 2@O must be in large excess to assure fully oxidized, high quality material, while in W CVD, low H@sub 2@ to WF@sub 6@ ratio (usually 4) is required to achieve good conformality in via filling. Second, gaseous species may undergo substantial wall reactions, which in turn depend on previous process history (e.g., in W CVD, HF and WF@sub 6@ condense on walls and subsequently desorb slowly). Third, the mass spectrometer ionizer provides a second reaction region (in addition to the wafer), contributing to the depletion of the reactants and occasionally generating the same products as the CVD reaction itself (HF in W CVD from H@sub 2@/WF@sub 6@ precursors). Fourth, the combination of wall adsorption/desorption and sensor reactions can lead to another extraneous source of products. In the H@sub 2@/WF@sub 6@ system sustained H@sub 2@ flow after the WF@sub 6@ flow is terminated leads to sensor generated HF utilizing the WF@sub 6@ desorbing from the walls. We illustrate these phenomena through both experimental and modeling results, and we assess key aspects of the general approach for multicomponent CVD systems.

3:40pm **MS-WeA6 Mechanisms for the Production of Atomically Flat Surfaces Studied by Scanning Probe Microscopy@footnote 1@***, **S.C. Langford**, R.F. Hariadi, J.T. Dickinson,* Washington State University

Chemical-mechanical polishing (CMP) is a critical step in the fabrication of integrated circuits, yet the complex interactions between chemical and mechanical effects in CMP are still not well understood. We examine layer by layer material removal and deposition under conditions of combined mechanical stress and chemistry using scanning probe microscopy (SPM), where the SPM tip serves as a model single asperity/abrasion particle. We focus on monolayer-deep etch pits on a model, biomaterial substrate, single crystal brushite (CaHPO@sub 4@@super .@2H@sub 2@O). Scanning across monolayer steps in undersaturated solutions at high contact forces produces distinct wear tracks due to localized double kink nucleation. Low contact force scanning in supersaturated solution produces localized deposition along steps in the scanned region. The latter suggests a novel method of producing atomically flat surfaces by mechanically controlled re-crystallization. These results allow quantitative models of wear and deposition to be developed and tested. @FootnoteText@ @footnote 1@This work supported in part by the NSF Surface Engineering and Tribology Program under Grant CMS-98-00230.

4:00pm **MS-WeA7 Investigation of Thermal Curing of an Organic Low-k Spin-on Dielectric by Variable-Angle Spectroscopic Ellipsometry***, **F. Yang**, W.A. McGahan,* Nanometrics, Inc.*; C.E. Mohler, L.M. Booms,* The Dow Chemical Company

As device features of ultra-large-scale-integrated (ULSI) circuits continue to shrink, a new type of dielectric material with a low dielectric constant k is needed for replacement of SiO2 as the insulating material between multi-level interconnects. Dow Chemical's SiLK* semiconductor dielectric@footnote 1@ has been investigated as a potential candidate for the low-k dielectric. SiLK dielectric thin films are formed by spin-on process, followed by a thermal curing process, which determines the mechanical, electrical, and chemical properties. A properly cured SiLK dielectric thin film offers a dielectric constant of 2.65, along with merits of high thermal stability, excellent gap-fill properties, high solvent resistance, and low moisture absorption. In this paper, optical properties of SiLK dielectric thin films cured at different conditions are characterized using variable-angle-spectroscopic elliposmetry. Correlation is found between the optical constants in the ultra-violet wavelength region, and the extent of the cure (cure time and cure temperature). Based on the relationship between optical constants of SiLK dielectric and its curing condition, a single-parameter empirical interpolation model is developed to describe the dispersion of SiLK dielectric's optical constants. Despite a single adjustable parameter, this interpolation model closely tracks the variation of SiLK dielectric's optical constants at different curing conditions. With this model, in-line monitoring the cure of SiLK dielectric thin films can be realized. @FootnoteText@ @footnote 1@ SiLK* is a trademark of The Dow Chemical Company.

4:20pm **MS-WeA8 Assessment of Quadrupole Mass Spectrometry as an In Situ HDP-CVD Process Diagnostic Technique***, **J.A.B. Van Hoeymissen**,* IMEC, Belgium*; C. Hughes,* BOC Edwards industrial resident at IMEC, Belgium*; M. Heyns,* IMEC, Belgium

Process control using in situ techniques is an attractive aid to semiconductor manufacturing. The potential of quadrupole mass spectrometry (QMS) has been assessed as an in situ sensing technique for a silicon oxide high density plasma chemical vapour deposition (HDP-CVD) process. In this paper it is shown that in situ measurements using mass spectrometry can play an important role in the areas of process monitoring, process control and process recipe optimization. The species present in the chamber were analysed via a gas sampling system, with pressure reducing orifice, installed just below the deposition chamber to ensure a representative, real-time, sensitive measurement. Correlation between in situ observations and oxide layer thickness was investigated. H@sub 2@O is an important reaction by-product of the deposition reaction. A direct and highly sensitive correlation between the H@sub 2@O+ signal and oxide layer thickness could be observed. In fact, this QMS signal could be used to monitor oxide layer thickness during deposition. In addition, the [H@sub 2@O+] was found to increase exponentially during deposition. During consecutive depositions of P-doped oxide (PSG) layers, the thickness of the first layer was systematically about 2% higher than the subsequent layers. In situ analysis was carried out monitoring the time resolved intensity of mass 34 (PH@sub 3@+) during the first three PSG depositions. This intensity was clearly higher during the initial phase of the first PSG deposition. The composition of the layers were analysed with SIMS. The results indicate the phosphorus content of the first layer is significantly higher during the initial phase of the deposition. These combined results indicate a higher initial [PH@sub 3@] in the deposition chamber during the deposition of the first PSG layer. These observations prompted an adaptation of the chamber conditioning and clean recipe preceding the first PSG deposition, resulting in the disappearance of the first wafer effect.

4:40pm **MS-WeA9 Determining Ion Flux and Ion Energy from Radio-Frequency Current and Voltage Measurements***, **M.A. Sobolewski,*** National Institute of Standards and Technology

To obtain optimal results from plasma processing, the flux and energy of ions incident on the substrate must be carefully monitored and controlled. Several diagnostic techniques are used to measure ion flux and ion energy, but these techniques are typically not very compatible with the processes and reactors used by industry. Methods have been proposed for determining ion properties from the applied current and voltage waveforms, which can be measured in commercial reactors. However, such methods are usually not very accurate because they rely on false or untested assumptions. Here, a new, more accurate method is presented which makes use of a complete model of the time-dependent ion dynamics in the plasma sheath. The model was validated by comparison to independent measurements of ion flux, ion energy, and time-resolved optical emission, for high-density discharges in an inductive GEC Reference Cell. Measurements were performed for discharges in Ar, Ar/SF@sub 6@, and Ar/Cl@sub 2@, for inductive source powers up to 370 W, rf bias powers up to 100 W, rf bias frequencies of 0.1-13.56 MHz, and pressures of 0.67-4.0 Pa. An analysis of the sensitivity of ion flux and ion energy results to model parameters will be presented, along with comparisons showing the improvement in accuracy obtained by the new technique.

5:00pm **MS-WeA10 Linking Process and Structure using Automated Analysis of AFM Images*, D.A. Chernoff*,** *D.L. Burkhead, C.S. Cook,* Advanced Surface Microscopy, Inc.

By volume of product, the optical disc industry is the largest nanotechnology activity today. On DVDs (Digital Versatile Discs), the smallest features are about 400 nm long, 320 nm wide, 120 nm high, with a track pitch of 740 nm. Consumers need optical discs whose electrical performance during playback is consistently within specifications. Existing disc analyzers report electrical test results and engineers respond to deviations by adjusting process variables. This method provides only indirect control because the process variables determine the microstructure of the master, stamper and replica and it is that microstructure which determines ultimate electrical performance. A method is needed to examine microstructure so that one can see how each process variable affects various aspects of microstructure and to see how each aspect of microstructure affects performance. Automated, high accuracy analysis of Atomic Force Microscope (AFM) images provides the missing link. We measured the following parameters: track pitch, bump height, bump width and length (at various threshold levels), bump length, and four sidewall slope angles, in each case reporting mean, standard deviation and other statistics. From each 10 um image of a DVD stamper, containing about 100 bumps, we tabulated about 1000 values. Bump width increased with bump length, correlating with a corresponding increase in amplitude with pulse duration when a finished disc is played. Where sidewall angle deviated from the norm, we reviewed the image data to identify the specific nature of the defect. The results were statistically robust not only for mean values, but also for standard deviations, so that we could compare process variation from different pieces of equipment. Thus, feature geometry will no longer be a hidden variable in the path between controlling production equipment and observing the good or bad electrical performance of a finished disc.

Topical Conference on Emerging Opportunities and Issues in Nanotubes and Nanoelectronics
Room 6C - Session NT+NS+EM+MS-WeA

Nanotubes: Growth, Characterization and Properties I

Moderator: S.B. Sinnott, University of Kentucky

2:00pm **NT+NS+EM+MS-WeA1 Making and Modifying Carbon Nanotubes*, R.E. Smalley,*** Rice University **INVITED**

The last year has produced exciting developments in our ability to produce and modify single wall carbon nanotubes (SWNT). New experiments have shown the feasibility of producing nanotubes in an efficient gas-phase process, sometimes having diameters down to approximately 0.6 nm. These methods involve chemical vapor deposition in high-pressure carbon monoxide. We are now pursuing this growth technique as a potentially viable means for cost-effective production of large amounts of SWNT. Development of new methods for purification and characterization of nanotubes has given new insight into their growth mechanisms. I will present new data on the morphology and length distributions of SWNT grown by traditional laser-oven methods, and outline new results on the behavior and characteristics of tube samples. Perhaps the most remarkable developments have been in the chemistry of SWNT as a new molecular species. Several groups have discovered means of covalent attachment of other chemical species to the tube ends and sidewalls. This derivatization significantly modifies the properties of SWNTs, permits the first true solutions of tube segments, and opens the door to a remarkable new realm of chemistry, materials science, and electronics.

2:40pm **NT+NS+EM+MS-WeA3 Roles of Fe, Co, and Ni in the Formation of Single-Walled Carbon Nanotubes and Encapsulated Nanoparticles*, J. Jiao,*** Portland State University

The preparation and structural properties of carbon nanoclusters synthesized by having the transition metals Fe, Co, and Ni react with carbon in three different methods were investigated comparatively with the focus on single-walled nanotubes and encapsulated nanoparticles. The carbon nanoclusters were synthesized first by the high temperature (~3000°C) and high carbon-content process of the conventional arc discharge, secondly by the high temperature but low carbon-content process of the modified arc-discharge, and finally by the relatively low temperature (~500°C) process of catalytic decomposition of carbon monoxide (CO). The samples were characterized with respect to morphology, internal structure, and related properties. The carbon nanoclusters prepared by three different methods appear quite different on the surface, but have features in common that this report emphasizes. The same element can apparently serve different functions, serving as catalyst under one set of condition, and being encapsulated into the growing cages in a different environment. The elements of the iron group (Fe, Co, and Ni) were known as catalysts for growing the single-walled nanotubes and strings of spherical particles in conventional arc discharge, but could be encapsulated into the graphitic particles in the modified arc discharge and the CO disproportion that this study demonstrates. It was found that variation of the metal-to-carbon ratio is required to make these elements assume the double roles of either catalyst or encapsulant. In this report, an assembly of growth phenomena of carbon nanoclusters indicating the roles of the Fe, Co, and Ni will be presented. The growth mechanisms of these structural phenomena in relation to the preparation conditions in particular to the ratio of carbon content in the reaction chamber during the preparation are discussed.

3:00pm **NT+NS+EM+MS-WeA4 Plume Diagnostics During Carbon Nanotube Production by Laser Ablation*, S. Arepalli,*** G. B. Tech./Lockheed Martin*; C.D. Scott,* NASA/Johnson Space Center

We report recent results of our plume diagnostics during carbon nanotube production by double pulse laser oven method. The evolution characteristics of different species in the plume from different regions of the laser ablated plume will be presented. Transient emission data is compared with plume images to formulate dynamics of plume expansion. Vibrational and rotational temperatures of C@sub 2@ and C@sub 3@ are estimated by comparison with computations. Excitation spectra of LIF are used to deduce ground state temperatures and populations.

3:20pm **NT+NS+EM+MS-WeA5 Synthesis and Integration of Carbon Nanotubes*, H. Dai,*** Stanford University **INVITED**

This talk focuses on controlled growth and properties of multi-walled and single-walled carbon nanotubes on catalytically patterned substrates. It will be shown that new possibilities are opened up in nanotube science and applications by synthesizing nanotubes at desired locations and orientations in ordered fashions. A recently developed chemical vapor deposition method for high quality single-walled nanotubes is combined with microfabrication methods to reliably integrate single-walled nanotubes into various electrical architectures. The transport properties of individual single-walled nanotubes will be presented. Functional nanotube electrical devices with advanced performances will be shown. Issues in further control of nanotube growth will be addressed.

4:00pm **NT+NS+EM+MS-WeA7 Growth of Vertically Aligned Carbon Nanotubes on Transition-metal Catalyzed Plain Silicon Substrates using Thermal Chemical Vapor Deposition*, Y.H. Lee,*** *Y.C. Choi,* Jeonbuk National University, Korea*; C.J. Lee,* Kunsan National University, Korea*; Y.B. Han,* Jeonbuk National University, Korea

Vertically aligned carbon nanotubes have been grown on a large area of transition-metal coated plain silicon substrates by thermal chemical vapor deposition method. We find that vertically aligned growth is critically dependent on the domain density in the transition metal cluster. Steric hindrance between nanotubes at an initial stage of the growth forces nanotubes to align vertically. Nanotubes are then further grown by the catalyst-cap growth mechanism. We also show emission patterns from aligned nanotubes. Our current approach of simple integration of stable field-emission displays on a large area puts a step forward to future display applications.

4:20pm **NT+NS+EM+MS-WeA8 Carbon Nanotube Tips: Structures and Properties***, **J. Han**, L. Yang, R.L. Jaffe,* NASA

A variety of structures and properties of carbon nanotube tips present challenges in understanding of electron tunneling and field emission of carbon nanotube materials. Topologically, a nanotube tip can be formed by joining a tube bulk and a cone or a half the fullerene. Different configurations can be resulted from arrangement of topological defects. Energetically favorable configurations are identified and classified using functional theory and molecular mechanics calculations. They are further used for electronic structure calculations based on tight-binding approaches. The location and intensity of localizes states at tips are studied as functions of the size and configurations of tips. The differences in localized stated between one and four-orbital calculations are also compared. Experimental results of carbon nanotube field emission properties are related to the calculations of the localized stated of nanotube tips.

4:40pm **NT+NS+EM+MS-WeA9 Electrochemical Deposition of Carbon Nanofilaments***, E. Anoshkina, **D. Zhou**, L. Chow, V. Desai,* University of Central Florida

Carbon nanofilaments are conventionally made from thermal catalytic chemical vapor deposition with carbonaceous gases as growth precursors. Based on their unique mechanical, thermal, and electrical properties, many applications of carbon nanofilaments have been realized in advanced technologies. We report here on a new method to prepare carbon nanofilaments, in which the nanofilaments have been made from organic solvents such as methanol through an electrochemical deposition process. Silicon wafers coated with Fe or Ni nanoparticles were employed as the electrodes, and the depositions were carried out at room temperature. It has been found that electrical field between the electrodes, conductivity of the solvent, and size of the catalysts play important roles in control of morphologies of the carbonaceous deposits. Furthermore, based on characterization of the nanofilaments using scanning electron microscopy, transmission electron microscopy, and energy dispersive x-ray spectroscopy, the formation and growth mechanism of carbon nanofilaments from the electrochemical deposition has been discussed.

5:00pm **NT+NS+EM+MS-WeA10 A Study on the Growth of Carbon Nanotubes with Respect to Process Conditions***, J.N. Srivastava, K.K. Awasthi, **C.D. Dwivedi**, G.N. Mathur,* Defence Materials & Stores Research & Development Establishment, India

Carbon nanotubes have been produced by graphite evaporation method in macroscopic quantities with reproducible results at different conditions. A study on the growth of CNT against the variation in Helium / Argon / Nitrogen pressure has been done and some interesting results are found with respect to geometry, density and alignment of the tubes. Total yield of the material is also found to be having correlation with the pressure and current. Material produced in different conditions has been characterized by XRD, SEM, TEM, TGA and FTIR techniques.

Plasma Science and Technology Division
Room 612 - Session PS+SS-WeA

Ion-Surface Interactions II

Moderator: C.I.H. Ashby, Sandia National Laboratories

2:00pm **PS+SS-WeA1 How Does Ion Bombardment Produce Enhanced Etching?***, **P.G.M. Sebel**[1], L.J.F. Hermans, H.C.W. Beijerinck,* Eindhoven University of Technology, The Netherlands

Etching of Si by XeF@sub 2@ is enhanced considerably by ion bombardment. The role of the reaction layer in this process is studied in a multiple-beam setup at room temperature. One of the main reaction products, SiF@sub 4@, is formed in this layer. During spontaneous etching a thick reaction layer with a chain-like Si@sub x@F@sub y@ structure is formed.@footnote 1@ From ion pulse experiments on a slow time scale (100 s), it is concluded that this reaction layer is depleted of fluorine by the ion bombardment. This thinner reaction layer leads to a lower spontaneous SiF@sub 4@ formation. The depletion of the reaction layer is supported by model calculations. Despite this lower spontaneous contribution, the release of reaction products on a depleted reaction layer under ion bombardment is enhanced by chemical and physical sputtering. However, to produce more reaction products, more reactants (XeF@sub 2@) have to adsorb. This raises the question: "How does ion bombardment cause XeF@sub 2@ to have an increased sticking probability".@footnote2@ From ion pulse measurements on a fast time scale (1 s) it is concluded that on a depleted reaction layer XeF@sub 2@ mainly sticks on dangling bonds with a sticking probability of 0.71. By contrast, on a thick reaction layer the adsorption probability of XeF@sub 2@ is determined by the much lower sticking probability of 0.08 on SiF@sub 2@ surface species. This explains the enhanced sticking probability under ion bombardment and shows that a depleted reaction layer is a prerequisite for enhanced etching under ion bombardment. @FootnoteText@ @footnote 1@ M.J.M. Vugts, M.F.A. Eurlings, L.J.F. Hermans, and H.C.W. Beijerinck, J. Vac. Sci. Technol. A 14, 2780 (1996) @footnote 2@Y. Tu, T.J. Chang, and H.F. Winters, Phys. Rev. B. 23, 823 (1981)

2:20pm **PS+SS-WeA2 Desorption Species from Fluorocarbon Film by Ar@super +@ Ion Beam Bombardment***, **M. Hayashi**, K. Karahashi,* Fujitsu Laboratories Ltd., Japan

Fluorocarbon films are formed on wafers and chamber walls in etching processes with fluorocarbon plasmas.@footnote 1,2@ Desorption species from them during etching have a lot of influences on Si device fabrication, for example, formation of side wall protection films in etched holes and fluctuation of plasma components in the near-surface region of a wafer. We succeeded in detecting the species that are desorbed from fluorocarbon films by ion bombardment. In this study, we constructed a new apparatus in order to investigate desorption species from fluorocarbon films. The measured fluorocarbon films were deposited on a Si wafer by exposing it to a C@sub 2@F@sub 6@ plasma in an inductively coupled plasma (ICP) reactor. The species desorbed by Ar@super +@ ion beam bombardment at a few keV into the films were detected using a quadrupole mass spectrometer (QMS). The film characteristics were evaluated simultaneously by x-ray photoelectron spectroscopy (XPS), and we discuss the correlation between the desorption species and the film characteristics. QMS spectra that were measured during the Ar@super +@ ion beam bombardment of the fluorocarbon films show many sorts of dissociated C@sub x@F@sub y@. CF@sub 3@@super +@ is a dominant QMS peak in the fragment pattern, and this indicates that CF@sub 4@ is a dominant desorption species. Besides, some large desorption species are recognized because of the detected large fragment ions of C@sub 3@F@sub 3@@super +@, C@sub 3@F@sub 5@@super +@, and so on. The ratios among CF, CF@sub 2@, CF@sub 3@, and CF@sub 4@ species, which were measured with the appearance energies, indicate that CF@sub 4@ is a dominant desorption species with the ratio of 80 % among them at the beginning of bombardment. However, continuous ion bombardment causes the CF ratio to increase instead of decrease in the CF@sub 4@ ratio. This demonstrates the change in film characteristics from F-rich to C-rich, which was evaluated by XPS measurement. Moreover, The formation of C-rich film also corresponds to a reduction in total amount of desorption species. @FootnoteText@ @footnote 1@K. Takahashi, M. Hori, and T. Goto, J. Vac. Sci. Technol. A 14, 2011 (1996). @footnote 2@T. Shirafuji, W. W. Stoffels, H. Moriguchi, and K. Tachibana, J. Vac. Sci. Technol. A 15, 209 (1997).

2:40pm **PS+SS-WeA3 NH@sub 3@ / Cl@sub 2@ Gas Assisted Etching of Copper with Focused Ion Beams***, **K. Edinger**,* University of Maryland

With the implementation of copper instead of aluminum as metallization layer in high performance integrated circuits, the use of gas assisted etching for focused ion beam (FIB) based failure analysis and circuit rewiring becomes increasingly important. In the present study the effects of exposing a copper substrate to a mixture of chlorine (Cl@sub 2@) and anhydrous ammonia (NH@sub 3@) during ion bombardment have been investigated. The exposure of the copper surface to chlorine or to NH@sub 3@-Cl@sub 2@ mixtures leads to the formation of a reaction layer. The thickness of this layer and its texture depends on the FIB parameters such as ion beam dwell time, gas pressure and the NH@sub 3@ to Cl@sub 2@ flux ratio. In addition, the experiments indicate that the formation of the reaction layer is enhanced in areas that have been previously exposed (i.e. damaged) with an ion beam. The etch yield shows a strong dependence on the ion beam dwell time and the gas flux. For short dwell times and low NH@sub 3@ and Cl@sub 2@ flux an up to 10-fold increase over physical sputtering could be achieved. With increasing Cl@sub 2@ flux the etch rate decreased and the maximum in the etch yield shifted to longer dwell times, indicating changes in the adsorption kinetics of the two gases.

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

3:00pm **PS+SS-WeA4 Guided Ion-beam Studies of Low Energy Cu@super +@ and Cu@sub 2@@super +@ Ion Interactions with Mo***, S.L. Anderson, A. Lapicki, K.J. Boyd, M. Aizawa,* University of Utah

Results of low-energy ion beam deposition of Cu@super +@ and Cu@sub 2@@super +@ on polycrystalline molybdenum at energies from 5 to 220 eV are presented. Thermodynamics in this system favor Cu diffusion to the surface. At low energies, Cu@super +@ is deposited on the surface with a sticking probability of ~0.6. As the energy is increased above 100 eV, stable subplantation of the Cu is observed. This threshold is substantially higher than expected for penetration; it seems likely that penetration occurs at lower energies, however, migration of the subplanted Cu to the surface is efficient. The results for Cu@sub 2@@super +@ are different in that subsurface copper is observed at energies down to 40 eV (20 eV/atom). This counterintuitive result is tentatively explained by the formation of complex defects which stabilize subplanted Cu. Possible defect production mechanisms are explored using variable-angle XPS, XAES and molecular dynamics simulations.

3:20pm **PS+SS-WeA5 Ion Solid Surface Interactions in IMP Cu PVD***, **X.-Y. Liu**, M.S. Daw, D.G. Coronell, V. Arunachalam, C.-L. Liu,* Motorola Semiconductor Products Sector*; J.D. Kress, D.E. Hanson, A.F. Voter,* Los Alamos National Laboratory

A thorough understanding of ion-solid surface interactions is important for predictive modeling of ionized mass plasma (IMP) Cu physical vapor deposition (PVD) at feature scales. Besides sticking coefficients and sputter yields, fundamental parameters such as angular distributions of sputtered and reflected particles, and thermal accommodation coefficient are also needed as inputs for the feature scale process simulator. Molecular dynamics (MD) simulations can be used to provide pertinent information and physical insights. In this presentation, we'll demonstrate our recent MD results for Ar+/Cu and Cu+/Cu systems, as a function of hyperthermal ion energies and impact angles. The issue of integrating different sticking coefficients for different surface "roughness" will be addressed, based on ion travel distance analysis. We have found that the sputtered particle distributions are not cosine, but can be described by a simple Gaussian-like formula. Reflection characteristics were also analyzed and compared with simple analytical assumptions. Finally, the existing trends in the MD results from the systems will be discussed in terms of interaction strength, ion energy and impact angle.

3:40pm **PS+SS-WeA6 Deposition and Etching Using Fluorocarbon Ions: Molecular Dynamics Simulations***, **C.F. Abrams**[1], D.B. Graves,* University of California, Berkeley

SiO@sub 2@ etch processes use fluorocarbon (FC) plasmas to achieve selectivity to Si, SiN, and photoresist. FC plasmas deposit films which slow the etching of these surfaces compared to SiO@sub 2@. Further etch process optimization hinges on understanding these films. Specifically, the mechanisms of Si etching through the FC overlayer remain matters of speculation. We used molecular dynamics simulations of FC ions impacting Si surfaces to understand this process. We developed a Si-C-F interatomic potential as an extension of our C-F potential.@footnote 1@ We simulated ion impacts at normal incidence onto a:Si surfaces up to fluences of 4x10@super 16@ cm@super -2@. We examined the effects of ion composition (CF@sub x@ for x=1,2,3) and incident energy (50 @<=@ E@sub i@ @<=@ 200 eV). At low fluences, all ions deposit FC overlayers with significant Si incorporation. We found that CF ions result in net CF@sub x@ deposition, while CF@sub 3@ ions result in net Si etching with a steady-state overlayer thickness that increased with E@sub i@. For example, for 100 eV CF@sub 3@, we observed deposition of 2 equivalent monolayers of C up to a fluence of 4x10@super 15@ cm@super -2@, followed by Si etching (0.065 Si/ion) through a FC film with a steady thickness of 9.5 Å and F:C of 1.6. For CF@sub 2@, the resulting steady-state, deposition or Si etching, depended on E@sub i@, with deposition being favored at the lower energies. A striking result of the simulations is the dynamic character of the FC film during Si etching. Although the composition and thickness of the layer are unchanging at steady-state, F and C atoms are constantly depositing and then being etched by subsequent ion impacts. This `recirculation' of F and C through the overlayer appears to play a key role in Si etching. Mechanisms of both initial film deposition and steady-state etching by FC recirculation will be discussed. @FootnoteText@ @footnote 1@ J Tanaka, C F Abrams, D B Graves. Subm, 46th AVS Intl Sym, 1999.

4:00pm **PS+SS-WeA7 Comparison of Thin-Film Nucleation and Growth from Ion-Beam and Cluster-Beam Deposition: Atomistic Simulations***, **T.A. Plaisted**, S.B. Sinnott,* University of Kentucky

Experimental efforts have examined the formation of diamond-like and tailored polymer films through beam deposition. The results show that strongly adhering hydrocarbon thin films can be generated through the impact of organic ions or small clusters with mica, diamond, or glass surfaces. To study the processes involved in the nucleation and growth of these films we have performed atomistic simulations of beam impacts. Specifically, classical molecular dynamics simulations have been used where the forces are calculated using a many-body, reactive, bond-order potential. Our goal is to better understand the dependence of the film structure the reaction conditions. The simulations show the atomic-scale mechanisms by which the films nucleate and reveal the conditions needed to tailor the structure of the film. They also provide a basis for comparing the nucleation mechanisms and film structures obtained from ion-beam and cluster-beam deposition. @FootnoteText@ This work is supported by the Petroleum Research Fund and the National Science Foundation (CHE-9708049). .

4:20pm **PS+SS-WeA8 Understanding Plasma Polymerization by Mass Selected Ions: 25 - 50 eV CF@sub 3@@super +@ vs. C@sub 3@F@sub 5@@super +@ Ion Modification of Polystyrene***, **M.B.J. Wijesundara**, L. Hanley,* University of Illinois, Chicago*; B. Ni, S.B. Sinnott,* University of Kentucky

Mass selected polyatomic ions beams can both create new materials similar to plasma polymers and elucidate polyatomic-surface collision mechanisms that are fundamental to plasma polymerization and etching. The fluorocarbon ions are studied here due to their technological relevance, the large number of previous studies on related systems, and their ability to illuminate several fundamental points in polyatomic ion-surface modification and plasma polymerization. Polystyrene has been chosen because it is a typical polymer surface whose lack of heteroatoms facilitates its surface chemical analysis. Previous experiments with 10 - 100 eV SF@sub 5@@super +@ and C@sub 3@F@sub 5@@super +@ indicated different chemistry with polystyrene surfaces.@footnote 1@ This work is continued here by examination of 25 - 50 eV CF@sub 3@@super +@ vs. C@sub 3@F@sub 5@@super +@ ion reactions with polystyrene surfaces using monochromatic x-ray photoelectron spectroscopy and molecular dynamics simulations. These two fluorocarbon ions display significantly different surface chemistry at these low kinetic energies that cannot be explained simply by eV/atom arguments. @FootnoteText@ @footnote 1@E. T. Ada, O. Kornienko, L. Hanley, J. Phys. Chem. B 102, 3959-3966 (1998).

4:40pm **PS+SS-WeA9 Surface Interactions of Plasma-Generated NH@sub 2@ Radicals***, E.R. Fisher, **J.R.D. Peers**, M.L. Steen,* Colorado State University

Ammonia plasmas are used in the microelectronics industry to deposit amorphous hydrogenated silicon nitride (a-SiN@sub x@:H) films. Thin films of a-SiN@sub x@:H are used as gate dielectrics and barrier coatings in microelectronic devices, capacitors in dynamic random access memory (DRAM) cells, and microfabrication of sensors and actuators. Using the imaging of radicals interacting with surfaces (IRIS) technique, we have performed a comprehensive study of the interactions of NH@sub 2@ with a variety of surfaces during NH@sub 3@ plasma processing. The substrates examined were Si(100), Pt, polyimide, polyethylene, and Teflon. In most cases, NH@sub 2@ scattering from the surface was greater than unity, indicating a production of NH@sub 2@ through surface reaction. Removal of charged species from the plasma molecular beam results in a decrease in the scattered NH@sub 2@ signal, indicating that the presence of ions in the plasma is responsible in large part for radical production at the surface. We have examined the dependence of the scattering signal intensity on applied rf plasma power and substrate temperature for all species. In addition, velocity distributions for NH@sub 2@ radicals scattering off the surfaces were measured. Using Monte Carlo simulation methods and assuming a Maxwell-Boltzmann distribution, we determine the translational temperatures of the scattered species. Species scattering off 300 K Si and Pt substrates have a translational temperature of 400±30 K, significantly higher than the substrate temperature, while the translational temperature of species scattering off the polymeric substrates tends to be closer to the substrate temperature. This suggests that the NH@sub 2@ radicals are coming to equilibrium with the polymeric substrates and not with Si or Pt. The temperature of the radicals in the plasma molecular beam itself is 512±8 K at 25 W applied plasma power, indicating that the radicals are cooling by collisions with the substrate surface.

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

5:00pm **PS+SS-WeA10 FT-IR and XPS Study of Plasma-treated Acrylic Coating Surfaces*, M.K. Shi,*** *G.L. Graff, M.E. Gross, P.A. Mounier, M.G. Hall,* Battelle Pacific Northwest National Laboratory

Polymer/metal multilayer structures have many potential optical, display, and packaging applications. A key issue for the successful processing of such multilayer stacks is obtaining good wetting and adhesion at each interface. Low-temperature plasmas have proven to be one of the most efficient technologies for such purposes. Moreover, the effects of plasma treatments are limited typically to the outermost surface layers and the process is fully compatible with the polymer/metal multilayers cluster tools. We studied the interaction of RF (13.56 MHz)plasmas with an acrylic (tripropyleneglycol-diacrylate)coating surface using FT-IR and XPS. The acrylic coating, with thickness varying from 100 Å to 2 µm, was deposited onto an Al metallized PET substrate by vacuum flash evaporation of the acrylic monomer and subsequent UV-curing. FT-IR measurements showed the destruction of initial ester (O-C=O) and ether (C-O-C) groups, and the ablation of H from C-H bonds after plasma treatments. These effects were accompanied by the formation of carbonyl (R-C=O) and/or acid (R-COOH) groups, and the development of graphite-like C-C structures. The spectral features are similar for N@sub 2@and O@sub 2@ plasma-treated surfaces, no N-containing absorption peaks can be identified for the N@sub 2@ plasma-treated surface. XPS measurements confirmed the loss of the ester (O=C-O) and ether (C-O-C) bonds with respect to the C-C (C-H) peak, and the formation of carbonyl groups. The spectra further showed that approximately 10% of atomic N have been incorporated into the surface after N@sub 2@ plasma treatment. These results showed clearly that FT-IR and XPS are complementary techniques for the characterization of plasma-modified polymer surfaces. The possible plasma/acrylic coating interaction mechanisms will be discussed.

Plasma Science and Technology Division
Room 609 - Session PS-WeA

Dielectric Etching

Moderator: V.M. Donnelly, Bell Laboratories, Lucent Technologies

2:00pm **PS-WeA1 Dielectric Etching : From Oxide to Low k Dielectrics*, P. Berruyer,*** LETI (CEA-Grenoble), France*; O. Joubert, D. Fuard,* CNRS-LTM Grenoble, France*; C. Verove,* ST-Microelectronics, France*; M. Assous,* LETI (CEA-Grenoble), France*; R. Blanc, H. Feldis,* ST-Microelectronics, France*; E. Tabouret,* LETI (CEA-Grenoble), France*; Y. Morand,* ST-Microelectronics, France **INVITED**

Dielectric etching for interconnection is one of the most critical processes of the ULSI technology. Up to now oxide has been used as inter-metal dielectric with an aluminum based metallisation. The well known issue of contact and vias etch process is the etch-stop phenomenon occurring in high aspect ratio structures, if highly selective process is required. The introduction of copper and thus dual damascene architectures, has increased the number of dielectric etch processes required in the fabrication of ICs. Moreover the level of difficulty of these processes has increased : aspect ratio can be higher than it is in contact and vias, holes but also lines can be etched and high selectivity to nitride is required. If the introduction of copper has led to a more critical oxide etch process, the introduction of low k material dielectrics will lead to a break off in dielectric etch processes. These low k materials can be either mineral or organic with various porosity. This paper deals with the different etching processes and plasma source required for these different dielectrics. First of all, process performances such as profile, selectivity, CD, trenching, µloading, etch stop, yield, plasma induced damage will be studied as a function of process parameters. We will point out that, if etch stop in high aspect ratio structures is the main issue in oxide etch, profile control is the main issue of the etching of low k polymer materials (SiLK). Mechanisms related with these 2 issues will be proposed. Process conditions required for the etching of aerogel materials will also be discussed. Then, taking into account the process performances and limitations obtained previously, different schemes of dual damascene structures with copper metallisation will be compared. @FootnoteText@ @footnote 1@ This work has been carried out in the frame of GRESSI consortium between CEA.G-LETI and FRANCE TELECOM-CNET

2:40pm **PS-WeA3 Surface Kinetics Study of Silicon Dioxide Etching with Fluorocarbons in Inductively-coupled Plasmas*, H. Chae*,** *H.H. Sawin,* Massachusetts Institute of Technology

High-density fluorocarbon plasma for silicon dioxide etching has various ion and neutral compounds. Depending upon the plasma condition, many difficulties arise such as RIE lag, inverse RIE lag, etch stop, and low selectivity of photoresist. Profile evolution modeling can provide understanding of these difficulties in etching as well as trenching, bowing, and faceting. In this research we have measured etching and deposition rates as function of ion bombardment energy, ion impinging angle, ion-to-neutral flux ratio, which are necessary for profile evolution modeling of silicon dioxide etching in inductively coupled plasma. In this work, ions and neutrals are extracted directly from plasma to differentially pumped side chambers. Surface reaction is studied by measuring etching and deposition rate with quartz crystal microbalance (QCM). At the same time, ion and neutral composition of the plasma is determined with mass spectrometer. Etching or deposition rate is measured with QCM as function of ion acceleration energy, ion-impinging angle, ion-to-neutral flux ratio, with various fluorocarbon plasmas. Ion flux is characterized by measuring physical sputtering rate of oxide with Ar plasma and neutral flux is characterized by measuring fluorocarbon deposition rate with CHF@sub 3@ plasma. Three different fluorocarbon plasmas-C@sub 2@HF@sub 5@, C@sub 2@HF@sub 5@ + C@sub 2@H@sub 4@F@sub 2@, C@sub 4@F@sub 8@- are studied for oxide and photoresist etching. Hydrogen rich chemistry - C@sub 2@HF@sub 5@ + C@sub 2@H@sub 4@F@sub 2@ (20%)- has high deposition rate at low ion bombardment energy less than 100V. That hydrogen rich chemistry has the smallest neutral flux and the largest ion flux among them while C@sub 4@F@sub 8@ has the largest neutral flux and the smallest ion flux at the same given power and flowrate.

3:00pm **PS-WeA4 Chemical Bonding Arrangement Approach for Selective Radical Generation in High-density, Low-pressure Fluorocarbon Plasma*, S. Samukawa*,** *T. Mukai,* NEC Corporation, Japan

Generally, SiO@sub 2@ etching is done with fluorocarbon gases so that a fluoropolymer layer is deposited on the underlying silicon to enhance the etching selectivity for SiO@sub 2@ over silicon and silicon nitride. CF@sub 2@ radicals have been used as the main gas precursor for polymer deposition, and CF@sub 3@@super +@ ions have been the dominant etchant for SiO@sub 2@ films. The CF@sub 3@@super +@ ions are mainly generated from CF@sub 3@ radicals. Thus, to realize high-performance SiO@sub 2@ etching, precise control of CF@sub 2@ and CF@sub 3@ radicals in the fluorocarbon gas plasmas is indispensable. In this paper, we discuss how the efficiency of radical generation is affected by the chemical bonding of gas molecules in the fluorocarbon gas plasma. We found that dissociation of the C=C and C-I bonds are 5 times and 6 times higher than that of the C-C bond in a fluorocarbon gas plasma. As a result, a C@sub 2@F@sub 4@ plasma could generate a higher density of CF@sub 2@ radicals than a C@sub 4@F@sub 8@ plasma. The CF@sub 3@I is also efficient source of CF@sub 3@ radicals (CF@sub 3@@super +@ ions). By changing the gas-flow ratio of the CF@sub 3@I and C@sub 2@F@sub 4@ mixture, the density ratios of CF@sub 2@ and CF@sub 3@ (CF@sub 3@@super +@) could be independently controlled and high performance SiO@sub 2@ etching could be obtained. The appropriate choice of chemical bonding in the fluorocarbon gases is a useful way to control the generation of radicals and ions for SiO@sub 2@ etching.

3:20pm **PS-WeA5 Flux Control for High-Aspect-Ratio Contact Hole Etching*, T. Tatsumi*,** *M. Matsui, Y. Hikosaka, M. Sekine,* Association of Super-Advanced Electronics Technologies (ASET), Japan

The relationship between SiO@sub 2@ etch rates and incident fluxes of reactive species in a dual-frequency (27/0.8 MHz) parallel plate system@super 1@ was evaluated by using various in-situ measurements tools, such as infrared laser absorption spectroscopy (IRLAS), quadruple mass spectroscopy (QMS), and optical emission spectroscopy (OES). The thickness and composition of a fluorocarbon (C-F) polymer layer on the etched SiO@sub 2@ surface was also measured by XPS. The SiO@sub 2@ etch rate in a large area depends on both the total amount of F (@GAMMA@@sub F-total@) in the C-F reactive species and the energy at the SiO@sub 2@ surface. @GAMMA@@sub F-total@ could be estimated from the net fluxes calculated by using F, CF, CF@sub 2@, and CF@sub 3@ radical densities.@super 2@ Reaction energy depends on the total amount of ion fluxes (@GAMMA@@sub ion@) which is a function of the plasma density (n@sub e@) at the sheath edge, the acceleration energy of ions (assumed to be peak to peak voltage V@sub pp@), and the energy loss in the C-F polymer layer. The thickness of C-F polymer layer (T@sub C-F@) could be varied by the amount of both the CF@sub x@ species and the oxygen radical in the incident fluxes, the oxygen out-flux from the SiO@sub 2@, @GAMMA@@sub ion@, and V@sub pp@. Excess CF@sub x@ reactive species induced the thicker polymer layer (>1 nm). The thick polymer layer of 5 nm corresponded to the energy loss of about 1 kV. When using @GAMMA@@sub F-total@ (CF@sub x@), @GAMMA@@sub ion@ (n@sub e@), V@sub pp@, and T@sub C-F@, we can conduct in-situ monitoring of the SiO@sub 2@ etch rate. The etch rate at the bottom of contact hole was also evaluated. The decrease in SiO@sub 2@ etch rate in the fine holes can be similarly explained by either the lack of etchant or the lack of reaction energy. In order to obtain the high aspect ratio contact holes, it is important to suppress the excess formation of the C-F polymer layer on the etched surface. Increasing the oxygen flux is one way to do this, however it decreases the selectivity to the resist mask and the SiN. Therefore, higher ion flux is needed to obtain an etching process that enables us to achieve the deeper contact holes with higher selectivity. @FootnoteText@ This work was supported by NEDO. @footnote 1@T.Tatsumi et al., Jpn. J. Appl. Phys., 37 (1998) 2394. @footnote 2@T.Tatsumi et al., J. Vac. Sci. Technol., A17 (1999); to be published.

3:40pm **PS-WeA6 Etching Chemistry and Kinetics of BCB Low-k Dielectric Films*, S.A. Vitale,*** *H.H. Sawin,* Massachusetts Institute of Technology

Etching of BCB has been performed in a high density inductively coupled plasma reactor using O2 + hydrofluorocarbons, O2 + F2, and O2 + Cl2 chemistries. The etch rates of the films and the selectivities over oxide are correlated to the flux of ions and reactive radicals to the wafer. Species identification and fluxes to the wafer are determined by mass spectrometry, two gridded ion energy and current analyzers, and a Langmuir probe. Etch rates at many points on the wafer are simultaneously measured using Full Wafer Interferometry. Etching yields as a function of ion bombardment energy, neutral/ion flux ratio, and ion impingement angle are quantitatively determined using a novel plasma beam / QCM system. It is proposed that in high density, low pressure plasmas, the etching rate can be limited by the radical flux and by the ion flux to the wafer under different conditions. The selectivity of BCB etching over oxide etching is greatest for etchant gas compositions of approximately 20-40% halogenated gas in oxygen. Selectivity over oxide greater than 20 has been realized with BCB etch rates over 1 um/min . The implications of these results for the integration of BCB as a low-K dielectric into a copper dual damascene architecture are discussed.

4:00pm **PS-WeA7 The Effect of Capacitive Coupling on Inductively Coupled Fluorocarbon Plasma Processing*, M. Schaepkens,*** *N.R. Rueger,* State University of New York at Albany*; J.J. Beulens,* ASM International, The Netherlands*; I. Martini, E.A. Sanjuan, X. Li, T.E.F.M. Standaert, P.J. Matsuo, G.S. Oehrlein,* State University of New York at Albany

Different inductively coupled plasma reactors differ in the amount of capacitive coupling, which may influence the plasma process in a non-obvious fashion. We performed a study of inductively coupled fluorocarbon plasmas in which the amount of capacitive coupling was systematically varied. It is found that the plasma density decreases while the electron temperature increases as the amount of capacitive coupling is increased at a constant inductive power level. The rate at which the dielectric (quartz) coupling window is eroded is found to scale with both the peak-to-peak RF voltage and the ion current density, and the dielectric window erosion is found to influence the resulting plasma gas-phase chemistry. The changes in these plasma electrical and chemical characteristics can, on their turn, have a large impact on the surface processes occurring in inductively coupled fluorocarbon plasmas, such as fluorocarbon deposition, fluorocarbon etching, SiO@sub 2@ etching and Si etching. An important result obtained in this study is that certain plasma etch processes, such as selective SiO@sub 2@-to-Si etching, can benefit to a certain extent from capacitive coupling effects.

4:20pm **PS-WeA8 High Density Plasmas Etching of Low Dielectric Constant Materials*, D. Fuard,*** CNRS, France*; O. Joubert,* France Telecom-CNET and CNRS, France*; L. Vallier,* France Telecom-CNET and CNRS

The etching step remains one of the key technological issue for low K integration in advanced CMOS technologies. We have studied the etching mechanisms of SiO@sub2@ masked fluorine free aromatic hydrocarbon polymer. Experiments are performed in a high density plasma helicon source operated at low pressure. Previous work has shown that the SO@sub2@/O@sub2@ chemistry, even if suitable for a good profile control, induces the formation of sulphur-based acids which may generate corrosion latter in the process. In this paper, we present results using sulphur free chemistries based on N@sub2@, H@sub2@ and O@sub2@. First, we have used X-Ray Photoelectron Spectroscopy (XPS) analyses to understand the etch mechanisms of the polymer. XPS analyses reveal that under high energy ion bombardment conditions, the polymer structure is strongly graphitized : C1s binding energy originating from the polymer shifts from 285 to 283.5 eV. The graphitization phenomenon is also dependent on the chemistry used. Without changing the plasma operating conditions, very reactive chemistries, such as pure O@sub2@, prevent the polymer graphitization whereas adding N@sub2@ to O@sub2@ may lead to a severe graphitization by decreasing the chemical component and favoring the physical component of the etch. Using appropriate gas mixture and plasma operating conditions, high aspect ratio contact holes are etched with a good profile control. XPS analyses of the etched structures reveal that the passivation layer formed on the polymer sidewalls is also strongly graphitized, suggesting that the passivation layer originates from the etch products. Some results obtained in other high density plasma tools using identical chemistries will be presented and general conclusion on polymer etching in high density plasmas will be drawn. @FootnoteText@ @footnote 1@ This work has been carried out within the GRESSI Consortium between CEA-LETI and France Telecom-CNET

4:40pm **PS-WeA9 A Mechanism of Oxide to Nitride Selective RIE*, T. Sakai,*** *T. Ohiwa,* Toshiba Corporation Semiconductor Company, Japan

In highly integrated ULSIs, selective etching of oxide to nitride has been widely used for Self-Aligned Contact (SAC) etching to increase the packing factor. It is known that the CF@sub x@ polymer formed selectively on the nitride surface suppresses Si@sub 3@N@sub 4@ etching. However the origin of selective CF@sub x@ polymer formation is not understood well. We studied the mechanism of oxide to nitride selective etching with focus on selective polymer formation. In CHF@sub 3@-based chemistry, the oxide etch rate decreased slightly from 540 nm/min to 470 nm/min when the cathode temperature was increased from RT to 120 °C. On the contrary, the nitride etch rate decreased abruptly from 720 nm/min at RT to 220 nm/min at 60 °C. XPS analysis showed CF@sub x@ polymer formation on nitride at 60 °C, but no CF@sub x@ polymer at RT. Increase of temperature increases the C/F ratio of the adsorbed species on the surface, therefore CF@sub x@ polymer formation is considered to be enhanced on nitride. Following this result, the temperature in actual SAC etching using C@sub 4@F@sub 8@/CO/Ar chemistry was increased from 20 °C to 70 °C, and the selectivity at the corner of nitride increased from 10 to 18. Further surface analysis of the nitride surface etched in C@sub 4@F@sub 8@/CO/Ar chemistry at 70 °C revealed that the etched nitride surface has C-N bonds. At low temperature, the nitride etching reaction forms volatile etching products of SiF@sub 4@, CFN, C@sub 2@N@sub 2@ and etc., leading to no CF@sub x@ polymer formation similar to oxide. However, at the higher temperature, the higher C concentration of adsorbed species on the nitride surface suppresses the formation of volatile CFN, resulting in remaining of CN compounds, and forms CF@sub x@ polymer. CO, which is the etching product in oxide etching, has a much higher vapor pressure compared to CN compounds. So a difference of CF@sub x@ polymer formation arises between the oxide surface and the nitride surface, resulting in selective etching of oxide to nitride.

5:00pm **PS-WeA10 SiON SAC Etching Technique Using C@sub 4@F@sub 8@/CH@sub 2@F@sub 2@/Ar Plasma for 0.18µm Technology and Beyond*, J.H. Kim,*** *J.S. Yu, J.S. Na, J.W. Kim, Y.S. Seol, J.C. Ku, C.K. Ryu, S.J. Oh, S.B. Kim, S.D. Kim, I.H. Choi,* Hyundai Electronics Industries Co. Ltd., Korea

A SAC technique using an oxynitride (SiON) layer as a contact oxide etch barrier has been developed for 0.18µm technology and beyond. Generally, a SAC which uses a SiN etch barrier for 0.25µm technology may exhibit some disadvantages such as wafer warpage, film lifting, transistor reliability degradation, large contact junction leakage, needs for additional anti-reflection coating (ARC) layer, and large parasitic capacitance due to its high dielectric constant. These demerits can be eliminated or improved when the SiON SAC technique is applied. But it is not easy to obtain an oxide etching process with a high selectivity to the SiON etch barrier because of oxygen component within the SiON layer. To overcome this problem, we intentionally introduced excessive Si during the SiON film deposition in order to increase the selectivity to SiON. The developed SiON layer plays the roles of ARC for wordline and bitline photo resist patterning, and side-wall spacer to build a MOS transistor as well as SAC oxide etch barrier. The contact oxide etch was done using C@sub 4@F@sub 8@/CH@sub 2@F@sub 2@/Ar in a dipole ring magnet (DRM) plasma. As the C@sub 4@F@sub 8@ flow rate increases, the oxide etch selectivity to the SiON increases but etch-stop tends to happen. In highly selective SAC oxide etching, it is very important to avoid etch-stop for a wide process window. It was reported that CH@sub 2@F@sub 2@ chemistry helps to widen the process window through its hydrogen effects.@footnote 1@ Our optimized contact oxide etch process showed the high selectivity to SiON larger than 25 and a wide process window (@>=@ 4 sccm) for the C@sub 4@F@sub 8@ flow rate. When the SiON SAC process was applied to a giga-bit DRAM of cell array, there was no short failure between conductive layers. @FootnoteText@ @footnote 1@J.H. Kim et al., The 193rd Meeting of Elecrochem.Soc., Abst. 183, 1998

Surface Science Division
Room 606 - Session SS1+EM-WeA

Semiconductor Surface Science

Moderator: C.T. Campbell, University of Washington

2:00pm **SS1+EM-WeA1 Electronic Transport Properties of Silicon Surfaces@footnote 1@***, **K. Yoo,*** University of Tennessee*; A.P. Baddorf,* Oak Ridge National Laboratory*; H.H. Weitering,* University of Tennessee

Most of our information about surface electronic properties has come from spectroscopic measurements and first principles electronic structure calculations. Direct measurements of transport properties of ultrathin films have revealed interesting physical properties, including quantum size effects. However, to correctly measure the surface or thin film conductivity, the conduction path through the bulk or substrate must be eliminated. We attempt to accomplish this by using crystalline silicon of "silicon on insulator''(SOI) material. Using STM, we have recently shown that 40 nm-thick Si(100) layers on SOI can be prepared with a comparable degree of structural perfection as the surfaces of bulk Si.@footnote 2@ For these SOI films, we also observed that at room temperature, LEED spots drift and gradually disappear during prolonged exposure to the electron beam, indicating that the ultrathin Si top layer is fully depleted of mobile carriers, i.e. non-conducting. This leaves surface states as the only conduction channel. We have measured the surface conductivity of the Si(100)2x1 reconstruction on SOI as a function of temperature and Si film thickness during exposure to molecular oxygen using a four-point probe technique in ultrahigh vacuum. The oxygen induced conductivity changes strongly depend on the Si film thickness (@DELTA@@sigma@=-1.75x10@super -5@(@ohm@@super -1@) for 40 nm and (@DELTA@@sigma@=-9.219x10@super -6@(@ohm@@super -1@) for 90 nm thick films at room temperature. Differences are also observed in the temperature dependence, with possibly significant surface contributions to total sheet resistance at low temperature. These results indicate a correlation between transport properties and surface states, which will be discussed. @FootnoteText@ @footnote 1@ Work supported by National Science Foundation(DMR-9705246). @footnote 2@ K. C. Lin et al, Appl. Phys. Lett. 72, 2313(1998).@footnote *@ Managed by Lockheed Martin Energy Research Corp.

2:20pm **SS1+EM-WeA2 Reinterpretation of the Scanning Tunneling Microscopy Images of Si(100) (2x1) Dimers-Observation on a Defect Free Surface***, **K. Hata,** S. Yasuda, H. Shigekawa,* University of Tsukuba, Japan

In this presentation, we demonstrate that STM images of dimers of Si (100) taken with usual tunneling conditions are seriously characterized by tunneling from surface resonances and bulk states. In some cases, tunneling from these states overwhelm tunneling from the surface states which STM is generally believed to observe. The key point was the success to fabricate an almost defect-free Si(100) clean surface (defect density ~0.1%), making observations at a very low bias possible (0.5V). STM images of the dimers at 80K and room temperature taken at such low biases showed several new features. (1) In the empty states, when the surface bias is above ~1.4V, regions between the dimers are observed. (2) At 80K, a bright row similar to that observed at room temperature is obtained, though a bright and dark (2x1) unit align alternatively along the dimer row direction. The brighter units observed at the high bias corresponds to the location of the upper atom. (3) In the filled states, each atoms of the dimers at room temperature when the surface bias is lower than ~-1V. Every time when the bias is increased, the STM images of the dimers would gradually revert to the usual bean-type image of dimers at ~-1V. High resolution CITS measurements and first principle calculations also showed consistent results. We revisit and refine the interpretation of the STM images of the dimers, insisting that tunneling from surface resonances and bulk states are very important. The new interpretation brings results of many experimental and theoretical researches into an unanimous agreement.

2:40pm **SS1+EM-WeA3 STM-Study of the Absorption of Molecular Oxygen on GaAs(100)***, **P. Kruse,** J.G. McLean, A.C. Kummel,* University of California, San Diego

There is currently a strong interest in making GaAs-oxide interfaces with very low defect densities to enable the use of GaAs-based FET technology. The interaction of oxygen with the GaAs surface plays an important role in this process. In this study, high-resolution scanning tunneling microscopy (STM) was used to image the chemisorption sites of molecular oxygen on the three most common reconstructions of the GaAs(100) surface, c(2x8), 6x6 and c(8x2) . All studies were performed at room temperature. The sticking probability was greatest on the surfaces with As-As dimer bonds. Even though the molecular oxygen prefers to initially react with the empty dangling bonds of the Ga atoms, after dissociation the oxygen atoms seek to form bridge bonds between an electron rich As atom from an As-As dimer and a second atom, either As or Ga. These dimerized As atoms do not exist in the c(8x2) reconstruction, hence the greater inertness of that surface. This is in contrast to the reaction of these surfaces with halogens which only need to form one bond per halogen atom and equally attack all reconstructions.

3:00pm **SS1+EM-WeA4 Chaotic-like Wavefunction Beating in Thin Silver Films with a Quasiperiodic Superstructure***, **C.-S. Jiang,** H. Yu,* University of Texas, Austin*; Ph. Ebert,* Forschungszentrum J@um u@lich, Germany*; X.-D. Wang, R. Diener, Q. Niu, C.K. Shih,* University of Texas, Austin

It has been shown that atomically-flat Ag films can be grown on GaAs(110) substrates. These surfaces with (111) orientation exhibit, in addition, a one-dimensional quasi-periodic superstructure. Taking such surfaces as a model system, we investigated the effect of quasi-periodic scattering potential on the electronic structure by using spatially resolved scanning tunneling spectroscopy. Quantum well states due to the z-confinement of the 2-D thin film are clearly observed as a function of thickness. In addition, we have observed very intriguing chaotic interference patterns The observation of chaotic interference pattern is found to arise from the quasiperiodic superstructure acting as scattering potential for the 2-D electronic system. Theoretical calculations of the electronic states of quasi-periodic structure are currently underway.

3:20pm **SS1+EM-WeA5 3C-SiC(100) c(4x2) Surface and Sub-Surface Probed by Core Level Photoemission Spectroscopy Using Synchrotron Radiation and by Scanning Tunneling Microscopy***, **V. Derycke,** H. Enriquez, P. Fonteneau, V.Yu. Aristov, P.G. Soukiassian,* Commissariat à l'Energie Atomique and Université de Paris-Sud/Orsay, France*; G. Le Lay,* CRMC2 - CNRS and Université de Provence, France*; C. Grupp, A. Taleb-Ibrahimi,* LURE, Université de Paris-Sud/Orsay, France

We investigate the 3C-SiC(100) c(4x2) reconstruction surface and sub-surface regions by Si 2p core level photoemission spectroscopy using synchrotron radiation at various photon energies and by atom resolved scanning tunneling microscopy (STM). The latter experiments are performed by tunneling into the empty and filled electronic states which allows to clearly identify both up- and down dimers (AUDD) [1] of the c(4x2) surface reconstruction. Contrary to earlier core level studies, we identify two surface shifted components at the Si 2p core level having the same intensity. These two Si 2p spectral surface features are clearly related to the up- and down-dimers (AUDD) of the c(4x2) surface reconstruction.@footnote 1@ In addition, two sub-surface shifted components are also found which shows that the sub-surface region is also significantly affected by stress far away from the outer surface, indicating the long range influence of the latter. The results also confirm that the c(4x2) reconstruction is terminated by one Si monolayer as already well established by various quantitative experimental investigations.@footnote 2@ These novel core level photoemission using synchrotron radiation and STM results further support the AUDD model of the 3C-SiC(100) c(4x2) surface reconstruction.@footnote 1@ However, they are clearly inconsistent with predictions of a "missing row asymmetric dimers" model (MRAD) recently proposed on the basis of ab initio pseudopotential calculations and STM image simulations.@footnote 3@ @FootnoteText@ @footnote 1@P. Soukiassian, F. Semond, L. Douillard, A. Mayne, G. Dujardin, L. Pizzagalli and C. Joachim, Phys. Rev. Lett. 78, 907 (1997). @footnote 2@see e.g. V.M. Bermudez, Phys. Stat. Sol. (b) 202, 447 (1997); and references therein. @footnote 3@3-W. Lu, P. Krüger and J. Pollmann, Phys. Rev. Lett. 81, 2292 (1998).

3:40pm **SS1+EM-WeA6 Mechanistic Studies of SiO@sub 2@ Deposition from TEOS / Ozone***, L.D. Flores, C. Tindall, **J.E. Crowell,*** University of California, San Diego

The low temperature deposition of SiO@sub 2@ from the reaction of tetraethoxysilane (TEOS) and ozone has been studied in-situ at atmospheric pressures. The studies were performed in a prototypical atmospheric pressure chemical vapor deposition (APCVD) reactor utilizing a commercial injector / vent assembly. The gas phase reactions were followed during deposition at 400°C using gas-phase transmission FTIR spectroscopy. Evolution of gas phase products during TEOS / O@sub 3@

reactions were compared and quite distinct from those observed during reaction of TEOS / O@sub 2@. The primary products produced upon ozonolysis of TEOS are acetic acid, formic acid, formaldehyde, carbon monoxide, carbon dioxide, and water. Mechanistic details of the deposition process were aided by model reaction studies performed in a gas cell using transmission FTIR spectroscopy. The model studies involved reaction of ozone with observed and potential deposition byproducts, such as acetaldehyde. The spectroscopic observations will be discussed with an emphasis on reaction mechanisms and the reactive pathways leading to the production of deposition precursors, and the influence of additives and byproducts on the morphological nature of SiO@sub 2@ film growth.

4:00pm **SS1+EM-WeA7 Microcalorimetric Heats of Adsorption of Metals on Metal Oxide and Si(100) Surfaces*, D.E. Starr*,** University of Washington*; D.J. Bald,* Intel Corporation*; J.E. Musgrove, J.T. Ranney, J.H. Larsen, C.T. Campbell,* University of Washington

Single crystal adsorption microcalorimetry has been proven to be a powerful method to study the heats of adsorption of gaseous atoms or molecules onto single crystal surfaces. Recently, a microcalorimeter has been built which possesses the capability to measure heats of adsorption of metal atoms onto single crystal surfaces as a function of coverage. A sensitive pyroelectric polymer is used to detect the heat released due to the adsorption of pulses of gaseous metal atoms, each containing ~2% of a monolayer, onto the surface. The microcalorimeter has been employed to study the energetics of film growth from the initial stages of deposition through the multilayer regime for metal on metal and metal on metal oxide systems. For the metal on oxide systems, an initial heat of adsorption which is much lower than the heat of sublimation of the metal is observed. This provides detailed insight into the thermodynamic driving force for the metal overlayer to form three dimensional islands. Auger electron spectroscopy was used to verify the growth morphology. In addition, the extension of this technique to study the heats of adsorption of metals onto silicon substrates allows the study of many systems important to metal-semiconductor contact technology. In order to accurately quantify the heats of adsorption, the metals sticking probability on the surface must be known. These have also been measured and will be discussed. In addition, via a thermodynamic cycle the adhesion energy of the metal to the substrate is obtained from the measured microcalorimetric heats of adsorption.

4:20pm **SS1+EM-WeA8 Nucleation and Growth of Hemispherical Grained Silicon*, D. Llera-Rodriguez*,** *E.G. Seebauer,* University of Illinois, Urbana

Hemispherical grained silicon (HSG) is a material beginning to find widespread use for electrodes in DRAM applications. HSG is formed by the chemical vapor deposition of amorphous Si, followed by a CVD "seeding" step under slightly different growth conditions to form nuclei for surface crystallization. Subsequent rapid thermal annealing to above 600°C induces the nuclei to grow into 100-nm hemispheres via surface diffusion, yielding an electrode with high surface area that increases the capacitance of the resulting device. In addition to the practical applications, however, HSG formation provides useful insights into the fundamental mechanisms of nucleation and growth in a two-dimensional amorphous-to-crystalline phase transition. For example, we can rationalize our experimental results for nucleation density in terms of a rate-equation-based nucleation theory. Furthermore, through a series of growth studies we show that subsequent growth of the initial nuclei can be well-described by a two-dimensional continuum model based on adatom-vacancy pair formation on the amorphous surface, together with diffusion of the atoms toward the growing hemispheres. The activation energy of 2.5 eV describing growth represents the sum of energies for adatom diffusion and surface vacancy formation on the amorphous surface. Somewhat surprisingly, this value for amorphous Si matches that measured by separate experiments for crystalline Si.

4:40pm **SS1+EM-WeA9 Characterization by STM of Interface between Silicon and Silicon Dioxide Layers Fabricated by Highly Concentrated Ozone*, H. Itoh*,** *A. Kurokawa, K. Nakamura, S. Ichimura,* Electrotechnical Laboratory, Japan

We will show that the silicon dioxide film fabricated by ozone exposure@footnote 1,2@ has smooth and flat interface keeping the original step and terrace feature. Hydrogen-terminated Si(100) wafer was used as a substrate. Flat surface was prepared by additional growth of epitaxial Si layers (thickness; 120 nm) on Si substrate, and atomic hydrogen was adsorbed on the surface for passivation. STM images showed that the prepared surface was atomically flat with wide terraces which is larger than 100nm. A high-concentration ozone generator was used to form ultra thin silicon dioxide film on the surface. The output from ozone generator was the mixture gas of ozone(30 vol%) and oxygen. The substrate was exposed to the gas at room temperature for half an hour to form silicon dioxide film. The thickness of the oxide film formed by the exposure was estimated to be 1 nm, which was analyzed from intensity of XPS Si-2p peaks. After the oxidation, the silicon dioxide fil! ! m was carefully removed by rinsing in HF solution to observe the interface structure. Slow etching rate in dilute HF solution(0.1%) was chosen to avoid uneven etching and the thickness was monitored every several minutes by XPS peaks to avoid overetching. The sample was inserted into ultra high vacuum(UHV) chamber and surface and interface was observed by scanning tunneling microscopy. STM images were obtained on the etched surface with monoatomic height resolution. Large terraces and few steps were observed in the STM images and surface roughness is estimated to be below 0.15 nm (rms.). This indicates that the silicon dioxide film was grown keeping the original step and terrace feature. The result suggests that Si was oxidized homogeneously and supports that the film was grown layer-by-layer mode. @FootnoteText@ @footnote 1@ A.Kurokawa et.al., Mater. Res. Symp. Proc.Vol. 513, p38, 1998, @footnote 2@ A.Kurokawa et.al., Mater. Res. Soc. Symp. Proc., 1999, in press

5:00pm **SS1+EM-WeA10 Significant Effects of Arsenic Ion Implantation on Si Selective Epitaxy by Ultra-High Vacuum Chemical Vapor Deposition*, T. Furukawa*,** *T. Nakahata, S. Maruno, Y. Tokuda, S. Satoh,* Mitsubishi Electric Corporation, Japan

Great attention has been paid on Si selective epitaxial growth for an application into ultra large scale integration. For the practical application, however, surface conditions of a Si substrate, which is affected by preceding process steps such as plasma etching and ion implantation, may have a great influence on growth behaviors. In this work, we have investigated the effect of low energy arsenic ion implantation on the Si selective epitaxy by use of ultra-high vacuum chemical vapor deposition. The substrates were prepared through conventional n-channel MOSFET fabrication sequence. In the arsenic ion implantation, dosage was varied from 0 to 4x10@super 15@cm@super -2@, while acceleration energy was fixed to be 10 keV. Before the Si growth, the wafers were cleaned by chemical wet etching, whereas chemical oxide was removed by diluted HF solution. The epitaxy was performed at nominal temperature of 600°C with a pure Si@sub 2@H@sub 6@ source gas. For a non-implanted wafer, island-like growth occurs. With sufficient dosage of arsenic ions, however, an epitaxial Si layer with excellent surface morphology was successfully grown. X-ray photoelectron spectroscopy measurements reveal that a thin SiO@sub x@ layer is formed below the substrate surface by a preceding plasma etching process. The growth mode change is interpreted in terms of reduction of the SiO@sub x@ layer by means of an additional sputtering effect of the ion implantation.

Surface Science Division
Room 607 - Session SS2-WeA

Gas-Surface Dynamics

Moderator: B.D. Kay, Pacific Northwest National Laboratory

2:00pm **SS2-WeA1 Dissociative Sticking of Small Oxidant Molecules on a Simple Metal; NO, O@sub 2@, CO and N@sub 2@ on Al(111)**, *H. Ternow,* ***I. Zori@aa c@****, B. Kasemo,* Chalmers University of Technology, Sweden

Motivated by our combined interest in molecular dissociation mechanisms at surfaces and early stages of surface oxidation, we are studying the dissociative sticking of small oxidizing molecules on Al(111). Hydrogen dissociation on metal surfaces has been clarified in detail by a close interplay between state resolved molecular beam experiments and calculated dynamics of dissociation on multidimensional potential energy surfaces. In contrast, dissociation dynamics of O@sub 2@ on simple metal surfaces, e.g. Al(111) and Ag(110, is not well understood. Molecular beam experiments indicate in both cases activated dissociation, while the calculated PES-s so far do not show such features. We have in this work investigated dissociation of several small molecules on Al(111) surface to elucidate the nature of the activation barrier and to explore these molecules' properties as oxidants for oxide film formation. The observed dissociative sticking for the two isoelectronic molecules, CO and N@sub 2@, is consistent with the presence of a very high activation barrier. In contrast, dissociation of NO and O@sub 2@ shows a rather low apparent activation barrier. Vibrational excitation of the molecules enhances dissociation. In the case of NO dissociation an energy dependent N/O ratio on the metal surface is observed. These features are discussed referring to the known symmetry and spatial extention of the frontier orbitals on the two species. The alternative - or complementary - view of the dissociation event, based on a harpooning mechanism, is also discussed.

2:20pm **SS2-WeA2 Chemical Selectivity and Remote Dissociation-ICl/Al(111)*, K.A. Pettus,*** *A.C. Kummel,* University of California, San Diego

We have investigated the chemical selectivity of ICl adsorption onto Si(111)-7x7, a high work function surface, and Al(111), a low work function surface. ICl chemisorbs onto these surfaces by two mechanisms, abstractive chemisorption and dissociative chemisorption. Abstractive chemisorption, in which one halogen atom of ICl bonds to the surface while the other is ejected into the gas phase, is the dominant mechanism for both the ICl/Si(111)-7x7 and the ICl/Al(111) reactions. Multiphoton ionization (205 nm MPI) spectroscopy and time-of-flight (TOF) mass spectrometry were used to determine that the ratio of iodine-selective abstraction to chlorine-selective abstraction is at least 10:1 for both the ICl/ Si(111)-7x7 and ICl/Al(111) reactions. However, the dynamics leading to the chemical selectivity are quite distinct. For the ICl and Si(111)-7x7 reaction, a transition state is formed by the donation of electrons from ICl to an empty dangling bond on the Si(111)-7x7 surface. Since the highest molecular orbital (HOMO) of ICl consists of atomic iodine orbitals, the iodine atom is the more reactive atom and chemical selectivity occurs. The ICl/Al(111) reaction occurs by a very different mechanism, remote chemisorption. In this process, an electron is harpooned from the aluminum metal surface to the lowest unoccupied molecular orbital (LUMO) of ICl. The adsorption of the electron transforms ICl into an excited repulsive state of the negative ion, ICl-. The LUMO primarily consists of atomic iodine orbitals; therefore, iodine again is the more reactive atom and ICl/ Al(111) abstraction favors the adsorption of iodine.

3:00pm **SS2-WeA4 Quantum-State-resolved Studies of Elastic and Inelastic Scattering of H@sub 2@ from Cu and Pd*, G.O. Sitz*,** *E. Watts,* The University of Texas, Austin

The scattering of H2 from Cu and Pd surfaces was studied using molecular beam techniques and quantum state-specific detection methods. A comparison is made for an unreactive case, H2(v=0)/Cu, and two reactive cases, H2(v=1)/Cu and H2(v=0)/Pd. Rotational excitation was observed in the scattering of H2(v=0) from Pd(111) and Cu(110) and was found to depend on the surface temperature. This rotational excitation occurred even when there was insufficient translational energy to account for the gain in rotational energy, indicating that part of the excitation energy is transferred from the surface to the molecule. The effect of vibrational motion in the H2/Cu system was studied by preparing the incident molecules in the single rovibrational state (v=1, J=1). The absolute survival probability of this state was measured along with the probabilities for rotational excitation and vibrational relaxation. This information is used to estimate the probability of dissociation of the vibrationally excited state. These results are compared with recent quantum dynamical calculations for the scattering of this particular state.

3:20pm **SS2-WeA5 Atom Scattering From Atomic Surfactants*, G.M. Nathanson*,** *J.A. Morgan, W.R. Ronk, M. Manning,* University of Wisconsin, Madison **INVITED**

Scattering experiments show that the rate of energy transfer between atomic gases and atomic liquids can be controlled by altering only the composition of the outermost surface layer of atoms. In the case of the 0.2% bismuth/99.8% gallium liquid alloy, the surface composition can be varied from a nearly pure Bi monolayer at temperatures near 290 K to 80% surface Ga at 900 K. This Bi surface enrichment is due to the much lower surface tension of pure Bi than of pure Ga. We find that impinging argon and xenon atoms lose nearly the same amount of energy in collisions with pure liquid Bi as with the bismuth-covered Bi/Ga alloy created at low temperatures. With increasing temperature, the rate of collisional energy transfer increases nearly linearly toward the value for pure liquid Ga as the surface Bi atoms are replaced by Ga atoms. These results suggest that the Ga atoms underneath the surface Bi atoms do not play a direct role in controlling the exit energies of the inelastically scattered Ar or Xe atoms; the rate of approach to gas-liquid thermal equilibrium depends only on the composition of the outermost surface layer.

4:00pm **SS2-WeA7 Molecular Beam Studies of the Extrinsic Precursor State: Trapping of Alkanes on Alkane-Covered Pt(111)*, A.F. Carlsson*,** *R.J. Madix,* Stanford University

Adsorbed species can significantly affect probabilities of adsorption of incident molecules. The classic studies of CO adsorption on metals lead to the concept of the extrinsic precursor state, and the analysis of Kisliuk of this process is well known. However, there few systematic studies of the dynamics of this process and the way in which properties of the adsorbed state affect adsorption. Using a liquid helium cryostat to achieve surface temperatures upward from 25 K and molecular beam methods, we have studied the adsorption probabilities of methane and ethane on Pt(111) surfaces presaturated by the adsorption of another alkane from a low pressure ambient. Firstly, methane adsorbs on the clean surface with near-normal energy scaling. On all covered surfaces, except that saturated by ethane, methane traps with probabilities ranging from 0.8 to 0.9, dependent on incident angle and energy. Generally, the trapping probability depends weakly on incident angle and energy. The weak dependence on incident angle is attributed to surface corrugation produced by the adsorbed alkanes. In the case of methane trapping on an ethane-covered surface a threshold to adsorption is observed. Below 16 kJ/mol the trapping probability remains very small, but above this threshold the trapping probability increases to 0.9. This "activated" molecular adsorption is quite dramatic. Ethane, however, shows distinctly different effects. The differences are attributed to size effects, not binding energy differences. These and other observations will be discussed.

4:20pm **SS2-WeA8 Influence of Rotational Energy on Adsorption Probability for a Physisorbed System: C2H4 on Ag(001)*, M. Rocca*,** *Luca Vattuone, U. Valbusa,* University of Genova, INFM, CSFBT-CNR, Italy

We show that the population of the rotational degrees of freedom of gas molecules affects their adsorption probability also for a physisorbed state. The effect, expected to be very general, is demostrated for the case of ethylene interaction with Ag(001) where we observe that the physisorption probability is suppressed for molecules produced with a hot nozzle, characterized by a sustantially larger rotational quantum number. Chemisorption of ethylene is observed for nozzle temperatures above 870 K and occurs in two phases characterized by different vibrational electron energy loss spectra. The barrier to chemisorption is in the vibrational degree of freedom as can be inferred by comparing pure and seeded beam data. At still larger nozzle temperatures fragmentation of ethylene upon adsorption is observed.

4:40pm **SS2-WeA9 Vibrational-State-Selected Studies of Gas-Surface Dynamics*, A.L. Utz*,** *L.B.F. Juurlink, R.R. Smith, P.R. McCabe, C.L. DiCologero,* Tufts University

A recently developed experimental technique uses state-resolved infrared laser excitation to probe dissociative chemisorption dynamics with quantum state resolution. We combine a supersonic molecular beam source, infrared laser excitation of methane molecules in the beam, and UHV surface spectroscopies to quantify the reactivity of gas-phase reagents excited to single, selected vibrational states. This approach permits independent and precise control over the translational and vibrational energy content of gas-phase reactants, as well as the character of their vibrational motion. We report on our use of this approach to unravel the dissociative chemisorption dynamics of methane on Ni(100). We find that methane molecules excited to the v=1 level of the antisymmetric C-H stretching vibration, @nu@@sub 3@, are up to 1600 times more reactive than are molecules in the v=0 level. Over a translational energy range from 16 to 68 kJ/mol, the sticking probability for these molecules increases from 3x10@super -5@ to 2x10@super -2@, which indicates that the @nu@@sub 3@ state is only responsible in part for the reactivity of a thermal distribution of vibrational states. We will also compare the efficacy of @nu@@sub 3@ excitation with other coordinates for energy deposition in the methane/nickel system.

5:00pm **SS2-WeA10 Reactive Scattering Dynamics of Fast Atoms with Hydrocarbon Surfaces: Initial and Steady-State Reactions*, T.K. Minton*,** *J. Zhang, D.J. Garton, J.W. Seale,* Montana State University

The interactions of energetic atoms with hydrocarbon surfaces are largely responsible for the degradation of polymeric materials in space and for the outcome of polymer etch processes. Molecular beam-surface scattering experiments show that non-equilibrium processes dominate both the initial and steady-state interactions when a hydrocarbon surface is bombarded with a beam containing fast oxygen atoms. Direct inelastic scattering is the most probable non-reactive interaction. The most likely initial interaction is gas-phase-like H-atom abstraction to form OH. Once formed, the OH may undergo further collisions and reactions with the surface, some of which produce H@sub 2@O. The initial reactive and non-reactive events may be described with a simple kinematic picture that allows us to determine the effective surface mass encountered by an incident O atom, as well as the fraction of the atom-surface collision energy (in the center-of-mass frame) that is converted into internal energy in the surface and in the recoiling gaseous species. During steady-state oxidation, CO and CO@sub 2@ are produced. Formation of these molecules is believed to account for the erosion, or mass loss, of a polymer under O-atom attack. The rate of CO and CO@sub 2@ production from the surface is significantly enhanced when high-energy (>9 eV) Ar atoms collide with a surface that is undergoing continuous oxidation. This observation suggests that collisional processes may be important in material etching.

Surface Science Division
Room 604 - Session SS3+NS-WeA

Islands, Clusters, and Steps

Moderator: J.C. Hamilton, Sandia National Laboratories

2:20pm **SS3+NS-WeA2 The Phase Diagram of a Self-Organizing Nano-Array*, K. Pohl***, *J. de la Figuera, M.C. Bartelt, N.C. Bartelt,* Sandia National Laboratories*; J. Hrbek,* Brookhaven National Laboratory*; R.Q. Hwang,* Sandia National Laboratories

Recent experiments show that in a submonolayer silver film on Ru(0001), a perfectly ordered array of nanometer-sized vacancy islands forms upon exposure to sulfur. By measuring the thermal vibrations of this equilibrium structure the forces responsible for the observed self-organization were identified and the elastic constants of the lattice derived.@footnote 1@ In order to develop a better understanding of the formation and ordering processes of this structure, we have explored the complete phase diagram of the vacancy island lattice. Via scanning tunneling microscopy we follow in real time the assembly of the hole lattice at different temperatures and S-Ag coverages. We find the hole lattice to be very robust against annealing cycles to 500 K. The final periodicity of the vacancy island lattice seems to be independent of the periodicity of the initial dislocation network in the strained silver film. This network only determines the initial etching sites for the S adatoms. The periodicity of the dislocation network in the clean Ag film depends on the Ag coverage. Beyond a threshold S-coverage, the array undergoes a phase transition to a periodic array of stripes. We will present a detailed study of the stability of these various novel equilibrium phases and identify the driving forces behind their formation. This work is supported by the Office of Basic Energy Sciences Division of Materials Sciences of the U.S. DOE (DE-AC04-94AL85000). @FootnoteText@ @footnote 1@K. Pohl et al., Nature 397, 238 (1999)

2:40pm **SS3+NS-WeA3 Tunneling on Ag and Au: Surface State Spectroscopy and Magic Molecular Clusters*, R. Berndt,*** RWTH Aachen, Germany **INVITED**

We use low-temperature scanning tunneling microscopy (STM) to investigate geometric and electronic properties of nanoscale structures. In this presentation, we discuss various aspects of the Ag(111) surface state such as surface state confinement to nanometer-sized islands, its interaction with isolated magnetic impurity atoms, and the first study of lifetimes effects on Shockley surface state electrons using low-temperature STM spectroscopy. Moreover, we report on observations of two-dimensional supramolecular clusters and chains which self-assemble upon deposition of 1-nitronaphthalene (NN) onto Au(111). NN molecules become 2D-chiral upon adsorption. Their handedness is determined from from high-resolution STM images and local density calculations. Modeling shows that hydrogen bonds cause the observed self-assembly. Clusters and chains mutually interact via electrostatic repulsion.

3:20pm **SS3+NS-WeA5 Step Energetics of Pb(111) Vicinal Surfaces from Facet Shape*, H.P. Bonzel***, *K. Arenhold, A. Emundts, S. Surnev,* Forschungszentrum Jülich, Germany*; P. Wynblatt,* Carnegie Mellon University

The formation energies of steps and kinks, the step stiffness and the step interaction energy of B-steps vicinal to (111) have been derived quantitatively from the equilibrium shape of small three-dimensional Pb crystallites supported on a Ru(001) surface. The crystallites were imaged by scanning tunneling microscopy and show (111) and (100) facets.@footnote 1@,@footnote 2@ The boundary of these facets is well defined in the STM images and was used to determine also the azimuthal dependence of the step free energy for vicinal (111) surfaces by employing an "inverse" Wulff construction. Taking the accepted value for the surface free energy of Pb, absolute step energetic quantities can be quoted for both A- and B-steps. The step stiffness is derived from the step curvature and the step energy. The entropic step interaction energy of B-steps at 440 K is calculated from the step stiffness. Furthermore, by taking into account the curved portion of the vicinal (111) surface normal to the direction of B-steps, which shows a Prokovsky-Talapov behavior,@footnote 2@ the total step interaction energy of B-steps is also obtained. The entropic and total step interaction energies of B-steps at 440 K are thus 2.3 meV/Å@super2@ and 7.9 meV/Å@super2@, respectively.@footnote 3@ The difference is largely attributed to the elastic dipole-dipole interaction. Calculations of the step and elastic step interaction energies using the embedded atom potential of Pb@footnote 4@ are currently underway and will be compared with the experimental data. @FootnoteText@ @footnote 1@ S. Surnev et al., J. Vac. Sci. Technol. A 16(1998)1059. @footnote 2@ K. Arenhold et al., Surf. Sci. 417(1998)L1160. @footnote 3@ K. Arenhold et al., Surf. Sci. 424(1999)271. @footnote 4@ H.S. Lim, C.K. Ong, F. Ercolessi, Surf. Sci. 269/270(1992)1109.

3:40pm **SS3+NS-WeA6 Control of Monolayer Island Vacancies on Pt(111) and their Impact on Surface Chemistry*, K. Nafisi***, *J. Samu, J.C. Hemminger,* University of California, Irvine

Michely and Comsa@footnote 1@ have demonstrated that argon ion sputtering Pt(111) at elevated temperature will create ordered monolayer deep island vacancies. We show, by varying the surface temperature parameter, that it is possible to control the size of these vacancies over the range of 30Å to 400Å. We have used a variable temperature, scanning tunneling microscope (STM) to quantify the formation of the island vacancies. We have also used the STM to investigate the dehydrogenation of a series of mono-olefins to form carbon particles at 700 K. The carbon particles were formed both on a clean, annealed, and on sputtered Pt(111) surfaces. The carbon particles are randomly distributed over the surface, and show no preference for formation at particular surface features such as step edges. Also, the formation of the carbon particles is not influenced by large monolayer island vacancies. However, on a surface, where smaller island vacancies have been formed, the carbon particles show a preference of forming on the terraces and not inside of the island vacancies. The difference in behavior between large vacancy islands and small vacancy islands (d @<=@ 40Å) can be explained if molecular diffusion across steps is slow and dehydrogenation products initially decorate the walls (steps) of the vacancy islands. We have also studied the impact of sputtering the sample prior to olefin adsorption with the incident ion beam at an angle away from the surface normal. The carbon particles formed on such surfaces are highly spatially aligned. @super *@This work was supported by the US Department of Energy, Office of Basic Energy Sciences. @FootnoteText@ @footnote 1@ T. Michely and G. Comsa, Nucl. Instr. and Meth., B82, 207 (1993).

4:00pm **SS3+NS-WeA7 Coalescence Dynamics of Small Pt Clusters on Pt(111) Surfaces: A Molecular Dynamics Study*, V. Chirita***, *E.P. Münger, L. Hultman,* Linköping University, Sweden*; J.E. Greene,* University of Illinois, Champaign-Urbana

The diffusion and coalescence of small clusters are fundamental intralayer mass transport processes, playing a crucial role during the early stages of thin film deposition and crystal growth. We use embedded-atom method molecular dynamics simulations to follow the kinetics characterizing these processes for compact, 2D Pt@sub 5@ and Pt@sub 6@ clusters on Pt(111), at 1000 K. Investigations are carried out for configurations consisting of clusters initially separated by a distance equal to that between second neighbors, in statistically independent runs of 10 ns each. Prior to coalescence, we observe that the intercluster separation distance is reduced via two pathways: net cluster diffusion, involving mechanisms which preserve cluster shape, and repeated cluster reshaping. Cluster diffusion occurs primarily via concerted gliding and reptation, a recently proposed diffusion mechanism for 2D clusters on (111) metallic surfaces. Cluster reshaping involves edge-diffusion and/or concerted dimer/trimer gliding. Our simulations reveal that cluster coalescence is achieved via complex dynamics. Clusters preserving their initial compact shape can coalesce via concerted gliding and form clusters with a high number of intracluster bonds. These larger clusters maximize the number of intracluster bonds in relatively short times, primarily via edge-diffusion. We observe for the first time, that during the fusion process, cluster-cluster interactions can induce cluster translations via sequential atom motion, through fcc/hcp bridge sites, within clusters. For clusters that reshape prior to coalescence, we observe that cluster-cluster interactions induce the transfer of single atoms, from either cluster, to sites neighboring both clusters, and thus create a "bond" between clusters. Once formed, we did not observe dissociation. In this case, the newly formed clusters have elongated shapes with narrow middle sections (1 to 2 atoms thick) and, as a result, the transition toward compactness is achieved over considerably longer times. Moreover, these clusters exhibit a variety of reconfiguration and migration events. Edge-diffusion, reptation and dislocation propagation are the competing diffusion mechanisms observed for clusters in this range.

4:40pm **SS3+NS-WeA9 Spontaneous Island Formation on the GaAs(001) 2x4 Reconstructed Surface*, P.M. Thibado*,** *V.P. LaBella, M. Anser, Z. Ding, D.W. Bullock,* University of Arkansas

Given the growing use of III-V semiconductor materials in wireless and high speed communication devices the preparation of atomically flat single crystal GaAs(001) surfaces was examined, since these devices are primarily fabricated using epitaxial methods . To achieve this, a state of the art molecular beam epitaxy (MBE) system with a novel temperature measurement system accurate to within ±2 @super o@C, has been combined, in situ, with a scanning tunneling microscope (STM). Surprisingly, when the GaAs(001) 2x4 reconstructed surface is annealed above a critical temperature (570 @super o@C), under a constant As@sub 4@ flux, it spontaneously forms one monolayer high islands covering one half of the otherwise flat terraces. This process is reversible and when fit to a free energy model yields information about the surface bonding energies. This work was funded in part by the National Science Foundation (DMR-9733994) and the Office of Naval Research (N00014-97-1-1058).

5:00pm **SS3+NS-WeA10 TiN(001) Epitaxy: An in-situ Temperature-Dependent STM and Level-Set Modeling Study***, S. Kodambaka,* ***P. Desjardins,*** *A. Vailionis, I. Petrov, J.E. Greene,* University of Illinois, Urbana*; D. Chopp,* Northwestern University

We have used in-situ temperature-dependent STM measurements during deposition and post-annealing combined with modeling to provide atomic-scale insights into surface morphological evolution during TiN growth. Epitaxial TiN(001) layers were grown by reactive evaporation onto MgO(001) at 700-950 @super o@C. Partial TiN monolayers (0.1-0.4 ML) were then deposited and in-situ high-temperature STM used to follow the coarsening and decay kinetics of single and multiple islands (Ostwald ripening) on flat terraces and in single-atom deep vacancy terraces. From these results, combined with finite-element solutions of the Gibbs-Thompson and diffusion equations, we obtain the activation energy for surface diffusion, the Ehrlich barrier energy, and the island line tension. We have also derived and implemented a level-set method for simulating the dynamics of island decay on time scales not accessible to experiment. Level-set methods are numerical techniques for computing the position of propagating fronts that can easily handle topographical changes as well as singularities including corner and cusp development. Our model includes geometry-dependent surface and edge diffusion, step-edge dynamics, and attachment/detachment rates. We compare our numerical results to in-situ STM time-sequence experiments under the same conditions. The results of the level-set calculations serve as a basis for a robust quantitative and predictive model for both microstructural and surface morphological evolution as a function of deposition conditions during polycrystalline TiN growth.

Thin Films Division

Room 615 - Session TF-WeA

Transparent Conductive Oxides

Moderator: P. Beauchamp, Optical Coating Labs

2:00pm **TF-WeA1 Recent Progresses on High Quality Tin-doped Indium Oxide (ITO) Films*, Y. Shigesato,*** Aoyama Gakuin University, Japan **INVITED**

Considerable efforts have been focused on depositing thin film tin-doped indium oxide (ITO) (thickness of 100-300 nm) with significantly reduced resistivity (lower than 1.0-1.5@Ao@10@super-4@ @ohm@cm) in order to accommodate the increasing technological demand for larger area flat panel displays with higher image quality. In this decade several breakthrough to deposit the low resistivity ITO with high reproducibility had been successfully carried out both for the evaporation-based and sputtering-based deposition processes applying quite different plasma techniques. As for e-beam evaporation (EB) processes, activation of the chemical reaction close to the substrate surface and low energy Ar@super+@ bombardment (10-30 eV) using tungsten electron emitters (EEIP) or an arc plasma generator (HDPE) were found to be effective for the low-resistivity ITO deposition. Whereas for the magnetron sputtering (SP) processes, lowering the sputtering voltage caused by lowering plasma impedance using the stronger magnetic field close to the cathode target or DC+RF technique was confirmed to be effective. Analyses on the crystallinity of the ITO films using XRD, FE-SEM, HREM and on chemical state of doped tin ions using ESCA, Transmission Mossbauer Spectra (TMS) were carried out to investigate how the deposition conditions affected the film structure and properties, and hence the reason for the low resistivity. It was clarified to be the key factors to deposit the very low resistivity ITO films that the doping efficiency of tin should be increased by decreasing the segregation at grain boundaries for the EB films, whereas the crystallinity should be improved by lowering the damages caused by high energy ion bombardments (more than 100 eV) during the SP deposition.

2:40pm **TF-WeA3 Electrical Properties and Surface Morphology of Heteroepitaxial Grown Tin-doped Indium Oxide Films Deposited by Molecular Beam Epitaxy*, N. Taga,*** Asahi Glass Co., Ltd., Japan*; Y. Shigesato,* Aoyama Gakuin University, Japan*; M. Kamei,* National Institute for Research in Inorganic Materials, Japan

Heteroepitaxial growth of Sn-doped indium oxide (ITO) and non-doped indium oxide (IO) thin films was carried out on optically polished single-crystal yttria-stabilized zirconia (YSZ) substrates by molecular beam epitaxy. The surface morphology of these epitaxial films was analyzed by scanning electron microscopy and the electrical properties were measured by four-point probe method and Hall-effect measurements. The ITO and non-doped IO films showed quite different surface morphology, suggesting that Sn acted not only as dopant but also as growth modifier for IO films. The surface morphology analysis on IO and ITO films revealed that a growth rate along the direction was enhanced by Sn doping. Resistivity (@rho@) of the epitaxial grown ITO films was 1.7E-4 @ohm@cm which was smaller than the @rho@ of polycrystalline ITO films (2.1E-4 @ohm@cm) deposited on glass substrate under the same deposition conditions. This result was consistent with the report on the heteroepitaxial films deposited by a conventional electron beam evaporation.@footnote 1@ The epitaxial ITO film deposited on YSZ(100) substrate showed higher carrier density N = 8.7E+20 cm@super -3@ and lower resistivity @rho@ = 1.7E-4 @ohm@cm compared with the one deposited on YSZ(111) substrate (N = 8.0E+20 cm@super -3@, @rho@ = 1.9E-4 @ohm@cm) deposited at simultaneously in the same batch. Such a difference between ITO(100)/YSZ(100) and ITO(111)/YSZ(111) implying that the crystal growth orientation should have large effects on the electrical properties. Sn concentration analyzed by X-ray photoelectron spectroscopy showed difference between the ITO(100) and the ITO(111), which was considered to be the one of the dominant factor for electrical properties. @FootnoteText@ @footnote 1@ N. Taga, H. Odaka, Y. Shigesato, I. Yasui, M. Kamei and T. E. Haynes, J. Appl. Phys. 80, 978 (1996).

3:00pm **TF-WeA4 Influence of the Target-Substrate Distance on the Properties of ITO Films Prepared by rf Reactive Magnetron Sputtering*, L.-J. Meng,*** Inst. Duperior de Eng. do Porto, Portugal*; M.P. Dos Santos,* Univ. Minho, Portugal

ITO films have been deposited onto glass substrates by rf reactive magnetron sputtering. The distance between the target and the substrate has been changed from 50 mm until 100 mm. The x-ray diffraction shows that the film prepared at large target-substrate distance has a strong orientation along [440] direction, and as the distance decreases, the intensity of the [440] peak decreases and the intensity of [222] peak increases. The electrical resistivity of the ITO films decreases as the target-substrate distance get small. This variation could be related with the change of the orientation of the films, the film, which has strong [222] peak intensity, has low electrical resistivity. The transmittance of the ITO films decreases and the optical band gap move to low energy direction as the target-substrate distance becomes small. In this work, all these phenomena will be discussed.

4:00pm **TF-WeA7 Properties of Fluorine-Doped Tin-Oxide Films*, X. Li,*** *S. Asher, R. Ribelin, P. Sheldon, T.A. Gessert,* National Renewable Energy Laboratory

Conductive tin-oxide (SnO@sub 2@) films are used extensively for transparent electrodes in electrochromic devices, flat-panel displays, and thin-film photovoltaic solar cells. SnO@sub 2@ with a tetragonal structure is naturally an n-type semiconductor because of a deviation from stoichiometry. With n-type dopants such as antimony, chlorine, and fluorine (F), very high electrical conductivity can be obtained. In this study, we investigated F doped SnO@sub 2@ films produced by low-pressure metal organic chemical vapor deposition. Tetramethyltin (TMT), oxygen, and bromotrifluoromethane (CBrF @sub 3@) were chosen as precursors. Due to the high volatility of CBrF@sub 3@ precursor, the F doping efficiency is strongly dependent on the substrate temperature and reaction chamber pressure. Secondary ion mass spectrometry (SIMS) analysis has revealed that the F doping level depends logarithmically on the CBrF@sub 3@ partial pressure, and the electronic concentration depends logarithmically on the F doping level. SIMS results also show that the F doping level remains constant through the film thickness, and that F does not diffuse from a doped layer into an undoped layer. Hall measurements show the electron mobility (µ) of the film increases with the doping level, which contrary to what is expected from ionized impurity scattering. For undoped SnO@sub 2@ films, the µ is ~1 cm@super 2@/V-s and electron concentration is low-10@super 18@/cm@super 3@. For F doped SnO@sub 2@ films, the electron concentration increases to mid-10@super 20@/cm@super 3@, and µ increases to 40 cm@super 2@/V-s. The optical and structure properties of doped and undoped SnO@sub 2@ films were also compared. Spectrophotometry demonstrated that the fluorine-doped film had a higher absorption than the undoped film. X-ray diffraction texture analysis revealed that as F is added to the film, the film orientation changes from random to a strong preference toward the (200) direction.

4:20pm **TF-WeA8 P-type Transparent Conducting In@sub 2@O@sub 3@ - Ag@sub 2@O Thin Films Prepared by Reactive Electron Beam Evaporation Technique***, J. Asbalter,* ***A. Subrahmanyam,*** Indian Institute of Technology, India

The transparent and conducting oxide thin films are all, so far, n - type. In the present investigation we report the results of thin films of silver doped In@sub 2@O@sub 3@ prepared on glass substrates by reactive electron beam evaporation at a substrate temperature of 180@super o@ C (at a chamber pressure of 2.5x10@super -4@ milli bar with oxygen) which have shown p-type conductivity under specific conditions. The evaporation rate is varied by changing the current (30 - 100 mA) to the electron beam. The starting material is the mixture of In@sub 2@O@sub 3@ and Ag@sub 2@O powder (of purity 99.99%). The composition of Ag@sub 2@O in the starting material has been varied from 0 to 100 Weight%. The electrical and optical properties of the films have been studied. The p-type conductivity has been observed in the films prepared at 80:20 composition evaporated at the rate of 65 Å per minute. The mobility and resistivity are 8.2 cm@super 2@volt@Super -1@sec@super -1@ and 22.5 ohm cm respectively. These films show an optical transparency of 38% at 500 nm and have an optical band gap of 3.95 eV. These data are being analyzed to understand the physics of the p-type conduction.

4:40pm **TF-WeA9 Mott-Schottky Analysis of Thin ZnO Films***,* ***C.F. Windisch****, G.J. Exarhos,* Pacific Northwest National Laboratory

Thin ZnO films have been prepared in our laboratory using both rf-sputtering and solution deposition routes. Processing parameters were found to have a marked effect on film conductivity. In addition, measured conductivity and infrared reflectivity could subsequently be enhanced by either chemical treatment in hydrogen gas at 400°C or cathodic electrochemical treatment in a neutral (pH = 7) phosphate buffer solution. While film conductivity and free carrier content usually are determined by Hall measurements, the present study focused on whether a conventional Mott-Schottky analysis could be used to monitor the change in concentration of free carriers in these films before and after chemical and electrochemical reduction. The Mott-Schottky approach is particularly promising for electrochemically modified films since the measurements could be made in the same electrolyte used for post-deposition electrochemical processing. Results of studies on sputtered pure ZnO films in ferricyanide solution were encouraging. Mott-Schottky plots were linear and gave free carrier concentrations typical for undoped semiconductors. Film thicknesses estimated from the Mott-Schottky data agreed with values calculated from reflectance measurements and confirmed by spectroscopic ellipsometry. However, studies on solution-deposited films yielded anomalous results. Mott-Schottky plots were nonlinear, apparently due to film porosity. A combination of dc polarization and AFM measurements confirmed this conclusion. The results suggest that Mott-Schottky analysis would be suitable for characterizing the dielectric response of solution-deposited ZnO films only if the effects of film porosity on the characteristics of the space charge region of the semiconductor were included in the analysis. This work was sponsored by the Office of Materials Science of the Office of Basic Energy Science, U. S. Department of Energy, under contract DE-AC06-76RLO 1830.

5:00pm **TF-WeA10 Direct Measurement of Density-of-States Effective Mass and Scattering Mechanisms in Transparent Conducting Oxides Using Second-Order Transport Phenomena***,* ***D.L. Young****, T.J. Coutts,* National Renewable Energy Laboratory*; V.I. Kaydanov,* Colorado School of Mines*; W.P. Mulligan,* Sunpower Inc.

TCOs have relatively low mobilities, which limit the techniques that may be used to explore their band structure via the effective mass, and limit the performance of the materials optically and electrically. The de Haas-van Alphen and other resonance techniques used to characterize the Fermi surface are not appropriate for TCOs that have a rather short relaxation time (i.e., low mobility). We have used transport theory to directly measure the effective mass and other fundamental properties of TCO films.@footnote 1@ The Boltzmann transport equation can be solved to give analytical solutions to the resistivity, Hall, Seebeck, and Nernst coefficients. In turn, these may be solved simultaneously to give the density-of-states effective mass, the Fermi energy relative to either the conduction or valence band, and the scattering parameter, s, which is related to the relaxation time and the Fermi energy. The little-known Nernst-Ettingshausen effect is essential for determining the scattering parameter and, thereby, the effective scattering mechanism(s). We constructed equipment to measure these four transport coefficients simultaneously over a temperature range of 30 - 350 K for thin semiconducting films deposited on insulating substrates. We measured the resistivity, Hall, Seebeck, and Nernst coefficients for rf magnetron-sputtered cadmium stannate (CTO) films@footnote 2@ with carrier concentrations in the range of 2-7x10@super 20@ cm@super -3@. We found that CTO is a highly degenerate semiconductor with a parabolic conduction band in this range of carrier concentration and that the density-of-states effective mass is 0.29±0.04 m@sub e@. This value agrees well with earlier studies of CTO@footnote 3,4@ but is, to our knowledge, the first direct measurement of both m@super *@ and s. Optical modeling of the effective mass agrees well with our directly measured value. Spectrophotometric analysis, resistance as a function of frequency, and mobility as a function of carrier concentration all indicate that grain-boundary scattering plays only a minor role in degenerate CTO. Early results indicate that the mobility reaches a maximum of nearly 80 cm@super 2@ V@super -1@ s@super -1@ for a carrier concentration of about 5x10@super 20@ cm@super -3@ when s approaches zero. The transition in the dominant scattering mechanism is indicated by a change in the sign of the Nernst voltage. @FootnoteText@ @footnote 1@ I.A. Chernik, V.I. Kaydanov, M.I. Vinogradova, and N.V. Kolomoets: Soviet Physics - Semiconductors, Vol. 2, No. 6 (1968) 645. @footnote 2@ X. Wu, W.P. Mulligan, and T.J. Coutts: Thin Solid Films, 286 (1996) 274. @footnote 3@ G. Haacke: Applied Physics Letters, Vol. 28, No. 10 (1976) 622. @footnote 4@ W. Mulligan: Ph.D. Thesis, Colorado School of Mines, Golden, CO (1997).

Vacuum Technology Division
Room 610 - Session VT-WeA

Dry Pumping Systems

Moderator: K.M. Welch, Consultant

2:00pm **VT-WeA1 Dry Vacuum Pumps - A Method for the Evaluation of the Degree of Dry***,* ***A.D. Chew****, R.P. Davis, R.A. Abreu,* BOC Edwards, U.K. **INVITED**

The drive towards dry vacuum pumping has occurred across the spectrum of vacuum applications from semiconductor manufacture to industrial processing. This brings with it a need to systematically evaluate and quantify the degree of cleanliness characteristic of any particular pump; currently there is no universally accepted method to perform this function. A methodology which has been developed for repeatable measurements of pump cleanliness will be discussed. It is based on residual gas analysis under carefully controlled pump conditions. This facilitates direct comparisons of cleanliness between pumps of the same and different design. Additionally it allows for the assessment of methods introduced to improve cleanliness.

2:40pm **VT-WeA3 Ebara AAS-series Screw-type Dry Vacuum Pump***,* ***Y. Watanabe****, R. Ward,* Ebara Technologies, Incorporated **INVITED**

A new screw-type dry mechanical vacuum pump from EBARA Corporation employs two-stage main pump screws and DC brushless motors to reduce energy consumption and the resulting greenhouse gas generation. The patented Zero Theoretical Clearance screw profile permits tighter mechanical fits and increases pumping efficiency.

3:20pm **VT-WeA5 Adapting Dry Vacuum Technology to Cu CVD Effluent Abatement in Integrated Circuit Manufacturing***,* ***J.R. Bottin****, D.G. Mrotek,* Leybold Vacuum Products **INVITED**

Developments in the manufacturer of IC's are driven by the need for a higher transistor density and increased speed. The semiconductor industry is aggressively pursuing techniques that enable 0.18 µm interconnects, with the goal of 0.13 µm by 2003 or sooner. Because of its low resistivity and high electromigration resistance, copper is the metal of choice for sub-quarter micron interconnects. New development will be required for copper processes including the abatement of copper and copper by-products. Chemical vapor deposition (CVD) of copper utilizing a liquid precursor is an efficient means for depositing seed layers of copper for high aspect ratio geometry. The reaction of the liquid precursor produces Cu, Cu(hfac)@sub 2@ and TMVS, which all have unique properties that can lead to premature dry pump failure and high abatement costs. A viable, environmentally friendly solution has been developed and is comprised of an optimized dry pump, inlet reactor, cooled exhaust collector and resin bed abatement device with integrated electrical control. The inlet reactor decomposes the residual liquid precursor leaving the tool and removes elemental copper. The residual Cu(hfac)@sub 2@ and TMVS remain in the vapor phase through the vacuum pump. The mixture is then cooled in an exhaust collector where Cu(hfac)@sub 2@ is condensed prior to entering the resin bed abatement device, where the TMVS is subsequently removed. The exhaust collector has been designed as a shipping vessel to transport the collected Cu(hfac)@sub 2@ back to the manufacturer for recycle, significantly reducing abatement costs. The system goal for 99% or greater removal of each component at the exhaust of the resin bed is presently being validated through beta-site testing. With copper interconnects representing the future of IC's, it is imperative that suppliers meet the process challenge posed by the use of copper. The system described above is a critical step toward meeting the challenge of Cu CVD effluent abatement.

4:00pm **VT-WeA7 Dry Pumping***, S. Doherty, F. Ramberg,* ***P. Annandale,*** Alcatel Vacuum Products **INVITED**

There are many reasons to convert from oil sealed, or so called 'wet,' vacuum pumping systems to those where no seal fluid or lubricant is exposed to the process gas. Among these are contamination, cost, and environmental impact. With certain deposition processes this conversion presents problems related to the phase change of the material pumped and its effect upon the pump and its handling by subsequent abatement systems. Alcatel has studied and characterized several processes that presented extremely difficult challenges in the conversion from wet to dry pumping. These conversions were ultimately successful due to an understanding of material properties and reactions possible within the pump and system hardware and the correct management of pump design and application. Alcatel will present process analysis, design features, and operating data that demonstrate how such classically difficult processes may be converted from wet pumping to dry pump systems. The analysis will include phase diagrams of the materials and products of reaction for the process, conductance calculations for the piping system, and the pumping speed requirements. A survey of dry-pump design types demonstrates why the process is difficult to achieve; and an in-depth discussion of the successful design is included. Finally, the data that demonstrate not only successful pump operation but, an accounting of process material is presented. What may be concluded from the presentation is what analysis techniques are available to determine whether a process will be difficult to convert from wet to dry pumping, and methods to predict what dry pump design type will yield success. Further, we will show the relative increase in reacted and reactive material exhausted from a dry pump over that from a wet system.

4:40pm **VT-WeA9 The Dry Pump in the Industrial Market***,* ***J. Scherbik,*** Stokes Vacuum Inc. **INVITED**

Dry pumps have been commonly used for some time in the semi-conductor market. This article discusses the pros and cons of a dry pump in the more traditional markets such as chemical, pharmaceutical, metallurgical, and vacuum coating. Different options will be presented along with a description of ancillary equipment. Cost of ownership is compared with more traditional types of vacuum pumps. Recommendations are included for pump sizing as well as discussing applications which might benefit from dry pumps.

Biomaterial Interfaces Group
Room 4C - Session BI-WeP
Poster Session

BI-WeP1 Self-Assembly of Tetraphenylporphyrin Monolayers on Gold Substrates*, A.L. Bramblett,* *M.S. Boeckl, T. Sasaki, B.D. Ratner, J.W. Rogers, Jr.,* University of Washington

The development of the next generation of medical implants involves attaching appropriate biorecognition molecules in the proper orientation and concentration on the surface of an implant, to prevent the cellular activation that leads to the foreign body response, and implant encapsulation. Porphyrin molecules are ideal for the development of a uniform monolayer, with controlled, optimal spacing of biorecognition groups. Self-assembled porphyrin monolayers on gold surfaces have been demonstrated with three custom synthesized alkylthiol substituted tetraphenylporphyrin molecules. Several techniques including x-ray photoelectron spectroscopy (XPS), ultraviolet/visible absorption spectroscopy (UV/Vis), scanning tunneling microscopy (STM), and grazing-angle infrared spectroscopy (GAIR) have been used to characterize the monolayers. XPS binding energy shifts in the S(2p) spectra reveal that the porphyrins are chemisorbed to the surface through a sulfur-gold bond.@footnote 1@ A red shift without a significant blue shift of the Soret band in the UV/Vis absorption spectra demonstrates that the porphyrin molecules are aligned on the gold surface in a side-by-side orientation.@footnote 2@ GAIR with a polarized light source, indicates that the porphyrin rings are oriented parallel to the gold surface. Round STM features, approximately 2 nm in diameter, correspond closely to the diameter of tetraphenylporphyrin (1.8 nm), and are distributed relatively evenly over the surface. Finally, XPS and UV/Vis coverage calculations show approximately monolayer coverage. Taken together, this data indicates the formation of self-assembled porphyrin monolayers. @FootnoteText@ @footnote 1@ Castner, D.; Hinds, K.; Grainger, D. W. Langmuir 1996, 12, 5083-5086. @footnote 2@ Osuka, A.; Maruyama, K. J. Am. Chem. Soc. 1988, 110, 4454-4456.

BI-WeP2 Protein Nanopatterning on a Gold/Aluminum Nanoarray*, C.K. Woods,* *Z.-P. Yang, A. Chilkoti,* Duke University

Protein nanopatterning has potential applications in the fabrication of multianalyte, proximal probe biosensors, genomic arrays, as well as modulation of cell-substrate phenomena. We have developed a technique to immobilize proteins on a surface with spatial resolution of around 100 nm. An ultraflat nanoarray of gold and aluminum is created on a silicon wafer by combining nanosphere lithography with "ultraflat template stripping"- a technique for creating ultraflat thin films of metal. The ultraflat gold/aluminum nanoarray is then incubated in a hexadecanethiol (HDT) solution, which forms a hydrophobic, self-assembled monolayer (SAM) on gold but does not adsorb onto the hydrophilic, native oxide layer on aluminum. We hypothesized that protein adsorption on a HDT-functionalized gold/aluminum nanoarray should occur preferentially on the HDT SAM, thereby allowing proteins to be nanopatterned on the 100 nm gold features. Formation of the HDT SAM on gold but not on aluminum was investigated separately on gold and aluminum substrates using contact angle goniometry, ellipsometry and atomic force microscopy (AFM). The model protein, Ribonuclease A, was found to adsorb preferentially to the HDT SAM on gold with a signal to background ratio of about 6. AFM studies of protein adsorption on HDT-functionalized ultraflat gold/aluminum nanoarrays are currently in progress as are experiments on extending this approach using SAMs presenting biological ligands.

BI-WeP3 Osteoblast and Monocyte Response to Nanometre Surface Topography In Vitro*, P. Hanarp,* Chalmers University of Technology, Sweden*; J. Rice, J.A. Hunt, J.A. Gallagher,* University of Liverpool, UK*; D.S. Sutherland, J. Gold,* Chalmers University of Technology, Sweden

It is well known that cells adhering to surfaces are influenced by micron-sized chemical and topographical features, but very little is known about cell behaviour on surfaces with smaller, nanometre-sized features. We have used a method based on adsorption of colloidal particles to produce surfaces with well-controlled nanotopography. Surfaces of silicon wafers, pre-coated with 30 nm of thermally evaporated Ti, were treated with aluminium chloride hydroxide giving a net positive charge at neutral pH. Then the surfaces were exposed to dilute aqueous solutions of 110 nm polystyrene particles, and the negatively charged particles adsorbed onto the positively charged surfaces randomly by electrostatic interactions. A submonolayer of particles was obtained with coverage controlled either by salt concentration in the colloidal solution for equilibrium adsorptions, or particle concentration and adsorption time in interrupted (non-equilibrium) adsorptions. To produce chemically homogenous surfaces, a film of titanium (82.5nm) was evaporated on top of the particle films. The titanium film was naturally oxidised in air. The response of primary human osteoblasts and monocytes to these surfaces has been investigated. The cells were cultured in contact with the samples, 1) flat titanium oxide, 2) 10% and 3) 20% coverage of 110 nm particles coated in titanium oxide, for 1 and 7 days. They were examined using fluorescent cytoskeletal staining, confocal microscopy and lactate dehydrogenase assays in conjunction with flow cytometry. At each time point, both osteoblasts and monocytes cultured on the flat titanium oxide and the 20% coverage surfaces showed a greater affinity for adherence than at the 10% surfaces. SEM analysis of the samples after cell culture showed that the surfaces are still intact. This work is ongoing, but these preliminary results indicate that osteoblasts and monocytes are influenced by nanotopography in vitro.

BI-WeP4 Gene Expression in Reaction to Micro and Nano-topography*, R. Hartley,* University of Glasgow, Scotland, UK*; A.S.G. Curtis,* University of Glasgow, Scotland, UK, Scotland

Cellular reaction to surfaces has particular relevance to engineering tissue constructs. Advances in microfabrication enabling production of structures with defined surface topography have facilitated our understanding of cell elongation, orientation and movement. The vastly differing cell morphologies and cytoskeletal arrangement on planar and topographical surfaces necessitate an investigation of adhesion, signal transduction and transcriptional regulation. This work investigates gene transcription in reaction to micro and nano-topography. In this study we used two differing methods Differential Display RT-PCR to assess gene transcription. The first relies on large scale total RNA isolation following in-situ cell lysis or transferral to suspension and subsequent lysis. The second follows the Klebe method of RT-PCR without RNA isolation, where although RT-PCR is generally carried out and optimised for 250 cells, the protocol is suitable for four cells. This method has particular significance for analysis of gene expression on small areas where cell number is limited. Methods: Sub-confluent tendon epitenon were trypsinised and seeded directly onto topographic and control substrata. For large scale total RNA isolation directly in-situ, or in suspension, GITC phenol/chloroform was used and RNA equilibrated using 260/280nm absorbance. The Klebe method used a -70@super o@ C freeze/rapid-thaw in the presence of RNase inhibitor allowing time for cDNA library creation. In each case cDNA libraries were amplified by PCR in the presence of @super 32@P dATP, then denatured and run on a 7M urea, 5% acrylamide electrophoresis gel. Separated isotopically labelled ssDNAs were viewed by autoradiography.Phage display systems were also used.

BI-WeP5 Do Oligoethyleneglycol Terminated Alkanthiols Induce Complement Activation?*, J.M. Benesch,* *S. Svedhem, S. Svensson, P. Tengvall,* Linköping University, Sweden

oligoethyleneglycol terminated alkanthiols with varying length of the ethylenglycol repeats were self assembled on gold surfaces. In Situ antibody ellipsometry techniques were used to study protein adsorption when the surfaces are incubated in serum or plasma. The results so indicate depositions of serum and also deposits of complement factors. This indicates that oligoethyleneglycol surfaces are not serum and plasma resistent. This behavior is dependent on the presence of calcium and the number of repeats in the ethylenglycol chain.

BI-WeP6 Hybridization of DNA Monolayers on Gold Observed In Situ with Surface Plasmon Resonance*, G.B. Saupe,* *M.J. Tarlov,* National Institute of Standards and Technology

The hybridization of end-tethered single-stranded DNA (ssDNA) probes on gold surfaces with ssDNA targets in salt solutions was monitored with surface plasmon resonance (SPR). SPR is a sensitive technique for measurement of angstrom-level changes resulting from surface DNA hybridization reactions. Surfaces derivatized with DNA are of interest for a variety of applications including genetic diagnostics, forensics, and infectious disease detection. In this study we have used a model system of thiol derivatized ssDNA probes self assembled on gold. The surfaces were subsequently treated with mercaptohexanol to passivate regions of unreacted gold and eliminate non-specific binding of the DNA. The effects of target ssDNA length, base pair mismatches, and the locations of the matching sequence within the target were evaluated in high salt conditions (1M NaCl). Probe coverages, hybridization efficiencies, and times needed for hybridization were measured. Recent data for the hybridization of mixed target solutions, where single basepair mismatched targets compete with exact sequence matched targets to hybridize a single probe, will be discussed.

BI-WeP7 Multivariate Comparison of Dodecanethiol Self-Assembled Monolayers Prepared by Microcontact Printing and Solution Assembly*, **D.J. Graham**, D.N. Price, S.L. Golledge, M.D. Garrison, T.C. McDevitt, B.D. Ratner,* University of Washington

In this study we show how exploring the entire TOF-SIMS spectra using multivariate statistics can enhance the analysis of a surface and bring to light details that are not obvious from univariate analysis. We have applied a PCA analysis to TOF-SIMS spectra of SAMs of dodecanethiol on gold prepared by solution assembly (assembly time: t =2sec,1min,5min,15min,30 min,1hr,24hr,6d) and microcontact printing (stamping concentration: c =0.001,1,5,10,50,100,200,1000mMol). PCA models from the TOF-SIMS negative and positive data were constructed. ESCA composition scans were also taken of all surfaces. Both univariate and multivariate comparisons were made between the solution assembled and stamped samples. The SIMS ratio sum[I(MolecularIons)]/sum[I(C-C3hydrocarbons)] and the ESCA C/Au ratio were used to compare the samples. Both methods found good correlation between samples in which a stamping concentration of 10-50 mMol produced SAMs similar to fully solution-assembled SAMs. This data is consistent with results from a similar stamping study using STM and contact angles by Larsen et. al.@footnote 1@ PCA analysis provided deeper insight into the two sets of samples. The scores from the first principal component (PC1) showed the similarities between the samples prepared by the two methods, though there was more scatter in the stamped samples. The second principal component (PC2) showed that some differences exist between the two preparations. Loadings from the second principal component showed that the differences in the samples were due mainly to the presence of oxidized species and silicone contaminants. Only trace amounts of Si (<1%) were seen in the ESCA spectra on some samples. The increase in oxidized species in the stamped samples may be due to the stamping procedure that was carried out in air. These differences may not be detected by other methods or by univariate analysis. @FootnoteText@@footnote 1@N. B. Larsen, H. Biebuyck, E. Delamarche, and B. Michel, J. Am. Chem. Soc. 119, 3017-3026 (1997).

BI-WeP8 Observation of Metal Clusters on Pancreatic Cells by Lateral Force Microscopy*, **A. Cricenti**,* Consiglio Nazionale Delle Ricerche, ITALY*; R. Generosi, S. Cotesta, M. Girasole, P. Perfetti,* Consiglio Nazionale delle Ricerche, Italy*; A. Congiu-Castellano,* Universita' di Roma La Sapienza, Italy

The interaction between pancreatic cells and metal ions have been studied at membrane level by Atomic/Lateral Force Microscopy in the repulsive regime of contact mode. The atomic force microscope can give both topographic and chemical (in lateral friction mode) informations on the cellular membrane of cells. Morphological characteristics of non infected cells and metal infected cells were easily imaged from fixed and dried cell preparations. Upon Cd2 and Zn ions uptake, the pancreatic cells don't change their morphology but the lateral friction images localized several metal clusters on the cellular membrane.

BI-WeP9 Microfabricated Cantilever Force Sensor for Measurement of Cell Locomotory Forces*, C.D.W. Wilkinson, A.S.G. Curtis, **B.W. Leslie**,* University of Glasgow, Scotland

Microfabricated cantilever force sensors are potentially capable of measuring attoNewton (10E-18 N) forces. Here, we propose a design for such a force sensor capable of measuring forces involved in cell locomotion. The cell guidance structures and cantilevers were fabricated as one integrated unit using dry-etching of polysilicon. Substrate used was a 300 µm thick (100) oriented silicon wafer coated on both sides with a 50 nm thick layer of silicon nitride. Wafers were cut into 25 mm squares. A 10 µm thick layer of isotropic polysilicon was deposited on one side of the wafer square. After patterning, the polysilicon layer was dry-etched to a depth of 10 µm to form cell guidance structures and a row of fifteen cantilevers along two opposing edges of the wafer square. Controlled etching of the silicon nitride layer ensured that cantilevers were released from the substrate while cell guidance structures remained in place. Cell guidance structures are designed to steer the cells toward the free end of the cantilever where deflection is largest for a given force. Cantilever dimensions (length=900 µm, height=10 µm, thickness=1 µm) combined with optical lever sensing of cantilever deflection are theoretically capable of measuring forces as small as 3 pN.

BI-WeP10 Surface Characterization of Microfluidic Devices*, **H. Canavan**, M.S. Ravenscroft, D. Ramaker,* George Washington University*; M.J. Tarlov,* National Institute of Standards and Technology*; J.J. Hickman,* George Washington University

Interest in the interactions of biomolecules with surfaces stems from various sources, including biocorrosion of ship hulls, the rejection of transplant materials in the human body, and biological fluids interactions with MEMS devices. A variety of chemical and physical factors affect biological fluid behavior in microchannels used in lab-on-a-chip devices. We report an investigation of the effect of polymer surface condition on microfluidic properties. The primary goal of this work is to correlate the electrophoretic flow properties through microfluidic channels of different polymer substrates with the surface condition of the polymers. While polymer substrates hold great promise for biological microfluidic applications, polymer surfaces are often poorly defined which can lead to irreproducible microfluidic behavior. To circumvent this problem, we are developing various protocols to control the surface functionality of polymers. Oxygen plasma treatment has been used to introduce oxygen functionalities that can then serve as active sites for covalent attachment of organosilane monolayers. XPS, SIMS, and contact angle measurements have been used to characterize as-is, oxygen plasma treated, and organosilane-modified surfaces of polystyrene, polymethylmethacrylate, and various co-polyesters. We will report on these measurements and preliminary fluid flow experiments.

BI-WeP11 Time-of-Flight SIMS Analysis of Micropatterned Biomaterial Arrays*, **S.L. Golledge**, M.D. Garrison, B.D. Ratner,* University of Washington

Micropatterned arrays of thin films, self-assembled monolayers and biomolecules are a critical enabling technology for the development of miniaturized biosensors and next generation biomaterials. Accurate characterization of the locally defined surface functional states is therefore crucial to the successful implementation of these novel approaches to surface engineering. We employed Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS), in both spectroscopic (static) and imaging modes to define and identify the spatial presentation of (1) bioactive polymeric materials prepared via radio-frequency glow-discharge (RFGD), (2) non-fouling organic thin-films patterned through microcontact printing (uCP), and (3) direct uCP matrix proteins important in biological wound healing. TOF-SIMS allowed characterization of both the bioactive species and the engineered reference regions, in addition to assuring that unwanted contaminant species were not present. Future prospects for TOF-SIMS analysis of micropatterned arrays will be proposed.

BI-WeP12 Atomic Force Microscope and Surface Plasmon Resonance Investigation of Polymer Blends of Poly(Lauryl Methacrylate) and 2-Methacryloyloxyethyl Phosphorylcholine-co-Lauryl Methacrylate*, **S. Clarke**, M.C. Davies,* University of Nottingham, U.K.*; V. O'Byrne,* Biocompatibles Ltd, U.K.*; C.J. Roberts,* University of Nottingham, U.K.*; J. Russell,* Biocompatibles Ltd, U.K.*; S.J.B. Tendler, P.M. Williams,* University of Nottingham, U.K.

In order to design new synthetic polymers for use in medical devices it is necessary to characterize the surface of the material to understand the interactions that occur when exposed to biological environments.@footnote 1@ Incorporation of phosphorylcholine (PC) into polymers has been shown to improve biocompatibility by suppressing unfavourable responses that occur on contact with tissue and bodily fluids.@footnote 2,3@ Polymers containing PC are currently in use as coatings for medical devices such as stents, catheters, or to fabricate contact lenses. As an alternative to synthesizing new PC-containing polymers, polymer blends offer the opportunity to investigate the surface properties of PC in new materials. Here, polymer blends of 2-methacryloyloxyethyl phosphorylcholine-co-lauryl methacrylate (PmMl@sub 6@) and poly(lauryl methacrylate) (PLMA) have been produced with varying ratios of the two components. The surface of the blends when coated onto silver has been characterised using X-ray photoelectron spectroscopy (XPS), tapping mode atomic force microscopy (TMAFM), and surface plasmon resonance (SPR). Analysis has revealed that the blends formed by the two polymers are immiscible and exhibit surface-segregation with nanometre-sized domains being formed throughout the range of the blends. The Pmml@sub 6@ is preferentially expressed at the surface of the blends leading to enhanced protein-resistant properties. @FootnoteText@ @footnote 1@ Davies et al, Chapter 4 in Biocompatibility:Assessment of Materials and Devices for Medical Applications. Braybrook, J (Editor) J. Wiley and Sons, 1997 @footnote 2@ Campbell et al (1994) Am. Soc. Artificial Organs J. 40 3 M853-M857 @footnote 3@ Ishihara et al (1991) J. Biomed. Mat. Res. 25 1397-1407.

BI-WeP13 Thermally Responsive Ultrathin Coatings by RF-Plasma Deposition*, **Y.V. Pan**, R.A. Wesley, R. Luginbuhl, R.M. Overney, D.D. Denton, B.D. Ratner,* University of Washington

Poly(n-isopropyl acrylamide) (pNIPAM) shows a lower critical solution temperature (LCST) of 31@super o@C in aqueous environment. At temperatures lower than the LCST, the polymer chains are well hydrated and fully extended. The polymer chains dehydrate and take on a more compact configuration above the LCST. This interesting phase transition behavior has been observed here with pNIPAM chains grafted onto solid surfaces by plasma deposition. In this presentation, thermally responsive coatings are prepared from glow discharges of NIPAM vapor. The synthesis and spectroscopic characterization (XPS, SIMS) of plasma polymerized NIPAM (ppNIPAM) will be presented. The ppNIPAM coatings obtained showed a remarkable retention of the monomer structure, and a phase transition at 31@super o@C in both water and air. The phase transition was measured by a novel AFM method. The water phase transition was surprising because of the expectation that the plasma environment would destroy the specific NIPAM structure associated with the thermal responsiveness. However, the transition in air was even more unexpected and suggests that adsorbed water on the AFM tip and at the polymer surface is sufficient to produce the phase change, even when the bulk of the polymer is unhydrated. Plasma polymerization of NIPAM represents a one-step method to fabricate thermally responsive coatings without specially prepared substrates and functionalized polymers.

BI-WeP14 Design of a Minimal Peptide for Adsorption to Hydroxyapatite and Cell Binding via an RGD Sequence*, **M. Gilbert**, C.M. Giachelli, P.S. Stayton,* University of Washington

In the natural remodeling of bone, the proteins that comprise the extracellular matrix play keys roles in the signaling of bone cells. These ECM proteins contain amino acid sequences such as RGD which are important for the adhesion of bone cells to the protein coated bone surface as well as the transmission of signals via outside-in integrin pathways. Many of the ECM proteins also contain stretches of acidic amino acid repeats, gamma carboxyglutamic acid residues, or high degrees of sulfation, glycosolation, or phosphorylation which aid in the adsorption of the protein to the mineral surface of bone. Despite the large body of knowledge on bone biology, most modern bone implant designs do not employ any control over the degree or specificity of protein adsorption to the surface of the implant which can result in lack of integration of the implant or encapsulation of the implant. However, by understanding how the biomineralization proteins bind to mineral surfaces and transmit signals to bone cells, minimal peptides can be designed which contain the features of strong mineral adsorption as well as integrin mediated cell adhesion and intracellular signaling to improve implant integration. A minimal peptide based on the mineral binding motif of salivary statherin combined with an RGD sequence was designed to bind and orient on hydroxyapatite surfaces. This fusion peptide (called N15-RGD) is capable of binding with high affinity to hydroxyapatite with the same Langmuir parameters as just N15 as well as maintaining alpha helical content in solution. N15-RGD, while immobilized on HAP, is also capable of binding cells specifically and in a dose dependent manner via the RGD sequence. The main integrin responsible for the binding of the cells to the RGD sequence is the @alpha@@sub v@@beta@@sub 3@ integrin. The N15-RGD peptide is thus oriented in such a manner that the RGD cell signaling sequence is still solution accessible to mediate integrin binding events.

BI-WeP15 Conformational Studies of Human Salivary Histatin-5 Bound to Hydroxyapatite Surfaces and Lipid Bilayers*, **M. Cotten**, J.L. Dindot, P.S. Stayton, G.P. Drobny,* University of Washington

Histatin-5 (hsn5) is a human salivary polypeptide found in the acquired enamel pellicle. The protein is histidine-rich and basic (DSHAKRHHGYKRKFHEKHHSHRGY), and possesses at least two important functions: control of HAP crystal growth and antimicrobial activity. Previous studies have characterized functionally important regions of the peptide sequence as well as some secondary conformation analysis in solution. Very little is known about specific hsn5/HAP and hsn5/lipid bilayer interactions and the conformation of the HAP-bound peptide. This knowledge is nevertheless necessary to better understand molecular recognition and structure-functions relationships. Our primary goals have been to characterize the conformation of hsn5 both free and bound to HAP crystals and lipid bilayers. Moreover, we have been interested in identifying interactions between the peptide and HAP by using solid state NMR techniques. Solid state NMR experiments that measure internuclear distances to sub-Angstrom accuracy have been performed to determine distances between two 13C carbonyl labels of adjacent amino acids and thereby constrain the conformation of the peptide bound to HAP. In addition, hisn5 with a 15N amide label has been incorporated into hydrated oriented lipid bilayers and used to determine the orientation of the peptide with respect to the bilayer.

BI-WeP16 Determination of Statherin N-Terminal Peptide Conformation on Hydroxyapatite Crystals*, **W.J. Shaw**, J.R. Long, J.L. Dindot,* University of Washington*; A.A. Campbell,* Battelle, PNNL*; P.S. Stayton, G.P. Drobny,* University of Washington

The interactions between proteins and inorganic crystals play an important role in the development and growth of hard tissues such as bone and teeth. Although many of these proteins have been studied in the liquid state, there is little information describing molecular recognition at the protein-crystal interface. Here we have used 13C solid state NMR (SSNMR) techniques to investigate the conformation of an N-terminal peptide of salivary statherin both free and adsorbed on hydroxyapatite (HAP) crystals. The torsional angle phi was determined at three positions along the backbone of the N-terminal 15 amino acid peptide fragment (DpSpSEEKFLRRIGRFG) by measuring 13C-13C distances between carbonyls in adjacent amino acids using the Dipolar Recoupling with a Windowless Sequence (DRAWS) technique. The peptides adsorbed to the HAP surface have an average phi of -85 degrees at the N-terminus (SS), -60 degrees in the middle (FL) and -72 degrees at the C-terminus (IG). The SS position corresponds to an angle typically associated with random coil peptides. The FL and IG positions correlate with angles known to be alpha-helical. These angles are approximately the same in the lyopholized peptides implying that secondary structure content of the peptide is retained upon adsorption to the crystal surface.

BI-WeP17 Tethering Phospholipid Bilayers to Porous Substrates, Progress Towards Biosensor Development*, **S.D. Ogier**, S.D. Evans, R.E. Miles,* Leeds University, UK

This poster concerns work currently being undertaken at Leeds University on the development of a biosensor based on ion channel conductivity. Our approach aims to span a lipid bilayer containing ligand gated ion channels across a hole micro-machined in a solid support. Electrodes either side of this hole allow the electrical properties of the bilayer to be monitored. The device employs a 0.1mm hole micro-machined in a solid support with a gold surface patterned around it. This enables us to modify the surface that the bilayer has to sit upon in order to create the conditions necessary for bilayer formation over the hole. Micro-machining of substrates has been used in a few cases to create architectures to suspend lipid bilayers and most of these use the solvent spreading method of Montal et al. or Langmuir Blodgett transfer. Although these techniques will be suitable for bilayer formation on the device, it is our aim to self-assemble the bilayer over the hole. This could be a very useful method of formation since it is a simple technique, however it does require the hole to have a similar diameter to the vesicle. The bilayer's electrical resistance is measured by applying a small (20mV) potential difference between two silver/silver chloride electrodes, one either side of the hole, and monitoring the current flowing between them. Although we have not yet achieved self-assembly over the holes, as they are too large, a bilayer formed using a solvent spreading method produced an electrical seal in the 10GOhm range.

BI-WeP18 Genetic Diagnostics Using SIMS Detection of Unlabeled DNA*, **T.J. Whitaker**, K.F. Willey,* Atom Sciences, Inc.

We are developing a new DNA chip technology that uses secondary ion mass spectrometry (SIMS) to determine genetic diagnostic information from unlabeled DNA. Genosensor chips, or DNA chips, typically contain arrays of single-stranded oligodeoxynucleotide (ODN) probes. Each probe has a known sequence and is attached at a specific site on the chip. The sequence of an unknown target DNA is determined by binding single strands of the target to the probes. This binding, or hybridization, ideally will occur only where the target sequence is complimentary to the probe sequence. Evidence of the binding is generally obtained by detecting fluorescent or radioactive labels attached to the target DNA. The new technology uses peptide nucleic acids (PNA) instead of ODNs for the probes. PNA is a DNA analog in which the phosphate and deoxyribose are replaced with polyamides. PNA binds to DNA with the same A-T, G-C rules as DNA/DNA hybrids but has slightly higher melting temperatures, offering the potential for greater discrimination between single-base mismatches. As opposed to DNA, which contains one phosphate along the backbone at each base, PNA contains no phosphorus. We have exploited this difference by using a simple SIMS analysis to detect molecular fragments containing phosphorus. The existence of phosphorus positively identifies the hybridization of unlabeled DNA to PNA probes. This method and a simplified, relatively inexpensive SIMS instrument are currently being developed under funding from the National Institutes of Health.@footnote 1@ @FootnoteText@ @footnote 1@This work is supported by the National Institutes of Health under contract 2 R44 HG01596-02. Its contents are solely the responsibility of the authors and do not necessarily represent the official views of the National Institutes of Health.

BI-WeP19 TOF-SIMS Analysis of the Candida Albicans Cell Surface*, **H. Shi**, B.J. Tyler,* Montana State University

The most common cause of failure for medical devices is infection, and the pathogenic yeast Candida albicans is the third leading cause of these infections. Adhesion is the first step in establishing an infection, the initial adhesion of microorganisms to synthetic polymer surfaces involves physicochemical interactions between molecules present at the polymer surface and those present on the cell surface. These interactions are not well defined, and insight into this area could lead to better material construction to effectively control the infection. The objective of this thesis is to study the initial adhesion event of C. albicans grown in glucose-based medium and galactose-based medium to Fluorinated Ethylene Propylene(FEP) and use Secondary Ion Mass Spectrometry(SIMS) to study the surface structural differences between these two cell surfaces with an attempt to correlate surface functionalities to the adhesion results. A freeze-drier with ultimate vacuum less than 1.00x10-9torr was constructed "in house" to freeze-dry cells for SIMS analysis. A filtration method was used to prepare a smooth layer of cells to be freeze-dried. Scanning Electron Microscopy showed that the freeze-dried cells appeared intact. High resolution SIMS spectra were obtained from these freeze-dried cell surfaces and Linear Discriminant Function Analysis combined with Principle Components Analysis were used to analyze the SIMS spectra. The results showed that the surfaces of glucose-grown cells contained more hydrophobic amino acid residues relative to those of galactose-grown cells. These hydrophobic amino acid residues probably promoted the adherence of glucose-grown cells to FEP surface. The results obtained in this study suggest that hydrophobic interactions are important in the initial attachment of C. albicans to FEP surface. The SIMS spectra presented in this study were the first report of the freeze-dried C. albicans.

Electronic Materials and Processing Division
Room 4C - Session EM-WeP
Poster Session

EM-WeP1 Comparison of Plasma Chemistries for Dry Etching of Ta@sub 2@O@sub 5@*, **K.P. Lee**, K.B. Jung, R.K. Singh, S.J. Pearton,* University of Florida*; C.C. Hobbs, P. Tobin,* Motorola

Inductively Coupled Plasma etching of Ta@sub 2@O@sub 5@ was performed in a variety of different chemistries, including SF@sub 6@ with additions of O@sub 2@, Ar, CH@sub 4@ or H@sub 2@ ; Cl@sub 2@/Ar ; N@sub 2@/Ar and CH@sub 4@/H@sub 2@/Ar. Etch rates up to ~1200 Å ú min@super -1@ were achieved with either SF@sub 6@ or Cl@sub 2@ based chemistries. Under these conditions the etch rates for Si were approximately 4-7 times faster, although equi-rate etching was achieved at low source powers and low halogen gas percentages in the plasma chemistry. The etched Ta@sub 2@O@sub 5@ surfaces were smooth (RMS roughness @<=@ 0.5 nm) over a broad range of conditions of source power, chuck power and process pressure. The etch rates with N@sub 2@/Ar and CH@sub 4@/H@sub 2@/Ar were an order of magnitude lower than with SF@sub 6@ or Cl@sub 2@. There was no effect of post deposition annealing on the Ta@sub 2@O@sub 5@ etch rates, at least up to 800@super o@C.

EM-WeP2 Study of the Impact of Time-Delay Effect on the Critical Dimension of Tugnsten Silicide/Polysilicon Gate After Reactive Ion Etching*, S.P. Lin, C.H. Ou, **S. Lee**, Y.C. Tien, C.F. Hsu,* Winbond Electronics Corporation, Taiwan

In the fabrication of submicron devices with high-density integration, the control of critical dimension (CD) of tungsten silicide/polysilicon gate becomes extremely crucial in device performance. To ensure a reliable gate patterning process, etching recipe with a very high selectivity is used to control the gate profile to be notching-free and vertical as well as keeping the gate oxide loss minimized. Besides the use of oxygen and chlorine-based chemistry in gate stack etching, HBr is also used to improve the selectivity of polysilicon to gate oxide. As a consequence of high selectivity, polymer residues become a major factor in CD control. It is believed that the presence of HBr in the plasma is responsible for polymer formation. HBr and its polymer residues may induce surface reactions to form thin oxide layers. Such a phenomenon has been observed if the wafers are not treated with HF vapor (for the removal of polymer residue) immediately after reactive ion etching (RIE) of the gate. The magnitude of the oxide film growth is proportional to the time delayed between RIE and HF vapor treatment. The sidewall thickness of the gate is also affected by the time-delay effect. The growth of oxide film on sidewalls can eventually affect the gate CD and thus the device performance. A simple reaction model for the growth of oxide film is proposed to explain the correlation between delayed time, CD bias, and product yield.

EM-WeP3 Effects of Deposition Temperature of Co Thin Films on (100)Si*, **H.Y. Huang**,* National Tsing Hua University, Taiwan, R.O.C.*; L.-J. Chen,* National Tsing Hua University, Taiwan, R.O.C., Republic of China*; W.F. Wu, R.P. Yang,* National Nano Device Laboratories, Taiwan, R.O.C.*; L.Y. Chen,* United Microelectronic Corporation, Taiwan, R.O.C.

Low resistivity silicide films have received a great deal of attentions because of their applications in ULSI in recent years. Low resistivty silicides have been widely used in source/drain as contacts. They reduce both the parasitic source/drain resistance and the contact resistance. Among all the silicides, NiSi, TiSi@sub 2@, and CoSi@sub 2@ are of the lowest resistivity. TiSi@sub 2@ is currently the most common silicide used as contact metal in IC industry. However, as devices are scaled down to deep submicron dimensions, it is difficult to transform TiSi@sub 2@ from high resistivity C49 phase to low resistivity C54 phase in small dimension features owing to the lack of nucleation sites. CoSi@sub 2@ is also of low resistivity and has been a promising candidate to substitute TiSi@sub 2@ for various processing advantages. In addition, its good lattice match with Si makes it possible to grow epitaxial silicide layer on Si. High temperature sputtering deposition (HTSD) was previously found to facilitate the phase transition from C49 to C54-TiSi@sub 2@. This method also reported as a new salicide technology for deep submicron devices to reduce the complicated process steps including TiN capping layers and preamorphization of substrate. In the present study, the Co films were deposited at different temperatures from room temperature to 550@super o@ C on (001) Si using UHV sputtering cluster tools. One- and two-step annealings were performed. TEM, XRD and AES were used to examine the samples. HTSD was found to improve both the thermal stability of CoSi@sub 2@ and CoSi@sub 2@/Si interface smoothness.

EM-WeP4 Growth of Ultra Thin Oxides of Silicon by Wet Oxidation Technique: Effect of Water Vapor Pressure*, **B. Viswanath Krishna**, K.N. Bhat,* Indian Institute of Technology, India

The rapid scaling down of silicon device dimensions has renewed interest in ultra thin oxides. The desirable properties of ultra thin oxides for gate dielectric applications are: very low defect densities, low charge trapping characteristics and high break down voltages. Although the ultra thin oxides grown by wet oxidation technique have higher breakdown strengths compared to that of dry oxide, the wet oxide has invariably large trapping characteristics and has problems in uniformity and surface roughness. In the present investigation, the effect of water vapor pressure (0.004 - 1.0 atm) on the ultra thin oxides of silicon grown by wet oxidation technique has been attempted. The wet oxidation is carried out in a quartz furnace maintained at 800@super o@C for 5 - 120 minutes. The ultra thin oxides are grown on single crystal CZ silicon wafers : n-type, (100) oriented, single side polished, of resistivity 1.0 - 10 @ohm@cm. The thickness of the grown oxides(3- 10 nm) has been estimated from the measured C-V characteristics and are also confirmed by ellipsometer measurements. The thickness of the oxide (60 minutes) seems to be rather independent at water vapor pressures till 0.05 atm. In order to understand the electrical performance of these thin oxides, Al/thin SiO@sub 2@ / n-Si MOS structures are fabricated and their Capacitance (C) - Voltage (V) (in the frequency range : 10 KHz - 1 MHz), conductance (G) - voltage (V) and Current (I) - Voltage (V) characteristics have been studied. Interface density (D@sub it@) and fixed oxide charge density (Q@sub f@) have been evaluated to asses the quality of the thin oxide layer. The breakdown voltage and the charge trapping characteristics have also been studied. The results indicate that reproducible ultra thin oxides can be grown with sufficient control by wet oxidation technique at reduced water vapor pressure.

EM-WeP5 Nanoscale Silicon Features Produced by Slow Highly Charged Ions*, **M.W. Newman**, A.V. Hamza, H. Lee, A.V. Barnes, T. Schenkel, J.W. McDonald, G.A. Machicoane, T. Niedermayr, D.H. Schnieder,* Lawrence Livermore National Laboratory

Phase transformations induced by intense, ultrafast electronic excitation from slow highly charged ions from the Lawrence Livermore National Laboratory (LLNL) Electron Beam Ion Trap(EBIT) have been studied. A 308 keV beam of Xe@super 44+@ (~51 keV of potential energy) was used to irradiate a 3 mm spot of clean float zone (FZ) silicon (100) (2X1) for a total dose of ~5x10@super 11@ ions. 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 becomes direct allowing for more efficient photon emission. Ex-situ room temperature photoluminescence (PL) spectra were measured using a high resolution grating spectrometer with an excitation wavelength of 379 nm from a Titanium-Sapphire laser. PL spectra from areas exposed to SHCI bombardment show a broad emission centered at 504 nm. This is consistent with emission observed from 1-2 nm silicon nanocrystals. No PL is observed from similarly prepared FZ Silicon samples exposed to beams of 308 keV Xe@super 27+@ (~10 keV of potential energy) and 5 keV Xe@super 1+@ with comparable doses. A series of sharp lines at 548 nm, 534 nm, and 530 nm are also present in the PL spectrum from areas exposed to Xe@super 44+@ which is characteristic of an excitonic series in nanometer size direct band gap materials. The deposition of potential energy from Xe@super 44+@ produces a phase transition in silicon surfaces at nanometer size level that is not produced from normal ion bombardment. This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under contract No, W-74505-ENG-48.

EM-WeP6 Formation of Ni-silicides on (001)Si with a Thin Interposing Pt Layer*, **L.-W. Cheng**, S.-L. Cheng,* National Tsing Hua University, Taiwan, R.O.C.*; L.-J. Chen,* National Tsing Hua University, Taiwan, R.O.C., Republic of China

As devices dimensions scale down to deep sub-micron regime, a linewidth dependence of sheet resistance was observe for TiSi@sub 2@. Among metal silicides, low resistivity NiSi is currently one of the two most promising silicides to replace TiSi@sub 2@ for the self-aligned technology of ULSI. NiSi possesses low resistivity, low silicon consumption, low processing temperature and relative insensitivity to the linewidth of the silicide. Previous works showed that the process window of NiSi can be extended to higher temperatures by nitrogen ion implantation. In the present work, the formation of Ni-silicides on (001)Si with a thin interposing Pt layer have investigated. TEM, XRD, SIMS and four point probe were used to analyze the characteristics of nickel silicide thin films. Pt addition was found to retard significantly the formation of nickel silicides on (001)Si. The process window of NiSi was extended to a higher temperature and the sheet resistance maintained the same low level in a wide temperature range. NiSi was observed to be the dominant phase for the samples annealed at 400-800 0C with a thin interposing Pt layer. Since nickel atoms are the dominant diffusing species in the Ni/Si binary system, the results implied that the diffusion of nickel atoms through Ni/Si interface is retarded by the presence of a thin interposing Pt layer.

EM-WeP7 The Interfacial Reaction between Ti and (001)Si with an Interposed Mo Layer*, **S.-M. Chang**,* National Tsing Hua University, Taiwan, R.O.C.*; L.-J. Chen,* National Tsing Hua University, Taiwan, R.O.C., Republic of China

Low resistivity TiSi@sub 2@ has been widely used in ultralarge scale integrated circuits because it possesses the low resistivity and compatibility with the SALICIDE processing. However, as the devices dimension shrinks to the deep submicron regime, it becomes increasingly more difficult to use thermal annealing to transform a structure from the high resistivity C49 phase to the low resistivity C54 phase due to insufficient nucleation sites of C54 phase at the C49 phase grain boundaries. Recently, a new and simple method for the reduction in the C54 transformation temperature was demonstrated. The formation temperature of the C54 TiSi@sub 2@ phase from the bilayer reaction of Ti on Si is lowered by about 100@super o@C by placing an interfacial layer of Mo between Ti and Si. However, the detailed mechanism is still not well understood. In the present study, high-resolution transmission electron microscopy (HRTEM) was utilized to study the interfacial reaction between Ti and Si with an interposed molybdenum layer. A thin amorphous TiSi@sub x@ layer was found to form and a thin Mo@sub 5@Si@sub 3@ layer was formed at the interface between the Si substrate and amorphous interlayer after 500@super o@C rapid thermal annealing (RTA) for 30 s. In addition, island formation was found to occur for Mo@sub 5@Si@sub 3@ after 535@super o@C RTA for 30 s. C49-TiSi@sub 2@ and Ti@sub 5@Si@sub 4@ phases were found to form simultaneously after 550@super o@C RTA for 30 s. The growth rate of amorphous TiSi@sub x@ layer was delayed with the presence of metallic interfacial layer. The formation temperature of the C49 TiSi@sub 2@ phase was also found to increase. The redistribution of Mo atoms, in the form of a ternary Ti-Mo-Si phase, after 550@super o@C RTA for 30 s, leads to the enhancement of the formation of C54-TiSi@sub 2@ by providing more heterogeneous sites needed for the transformation from C49- to C54-TiSi@sub 2@ phase.

EM-WeP8 Characterizing and Modeling the Electronic Conduction in CrB2-SiC-Si Thin Films*, **F. Wu**,* Medtronic, Inc.

Characterizing and modeling the electronic conduction in CrB2-SiC-Si thin films The CrB2-SiC-Si material system is used in thin film resistors in very large scale integrated circuits application. The films are sputter deposited onto dielectric substrates from composite target using various reactive gas mixtures. The microstructure of the sputter deposited CrB2-SiC-Si films is characterized by TEM as a distribution of darker ‘island’ regions within an lighter ‘boundary’ medium. In a wide range from 10-3 to 103 ohm -cm, the film resistivity is found as a function of the CrB2, Si and N composition. A model is proposed in this paper and computer simulation is perform to model the film resistivity behavior.

EM-WeP9 Silicon Nano-dots Fabricated on a Si(100) Surface via Thermal Nitridation and Oxygen Etching Reactions*, **J.S. Ha**, K.-H. Park, W.S. Yun,* ETRI, Republic of Korea

We have fabricated silicon nano-dots with a very uniform size distribution on a Si(100) surface via a thermal nitridation followed by an oxygen etching reaction. Nitrogen gas was exposed to a clean Si(100) surface at 800 @super o@C and this surface was subsequently reacted with O@sub 2@ gas at 700 @super o@C under an oxygen partial pressure of 1x10@super -7@ Torr. Scanning tunneling microscope (STM) measurement of the surface morphology showed that silicon nano-dots with an average size of 5 nm were formed as a result of selective oxygen etching of silicon surface. It is considered that nanometer-scale silicon nitride islands worked successfully as masks for the oxygen exposure at high temperatures. The number density of silicon nano-dots is estimated to be 1 x 10@super 12@ / cm@super 2@. Reduction of the nitridation temperature to 700 @super o@C resulted in the similar surface features with a little bit smaller sizes, indicating that silicon nitride islands formed even at this temperature can be successfully used as masks for oxygen exposure. Further investigation of the post-annealing effect on the resultant surface morphology showed that the coalescence of small sized silicon nitride islands into larger ones, which was clearly observed in the case of Si(111) surface, was not noticeable on the Si(100) surface. Therefore, uniform and small size distribution of Si nano-dots could be obtained on the Si(100) surface. In this paper, we will also discuss on the underlying reaction mechanisms based upon experimental results. This study suggests a simple but efficient fabrication method of silicon nano-dots using gas-surface reactions on the silicon surface in an ultra-high vacuum system.

Manufacturing Science and Technology Group
Room 4C - Session MS-WeP

Poster Session

MS-WeP1 Effects of Trapped Charges on Hg-Schottky Capacitance-Voltage Measurement of N-type Epitaxial Silicon Wafers*, Q. Wang, **D. Liu**, J.T. Virgo,* Mitsubishi Silicon America Corp.

The accurate carrier concentration profiling is very critical during silicon wafer process such as dopant profiling measurements of epitaxial layer or ion implanation etc. The mercury probe (Hg-Schottky capacitance-voltage (CV)) is a standard method in this application. This method is however, very sensitive to the silicon wafer surface condition and is a challenging issue in semiconductor industry. A poor Schottky contact will produce an erroneous and misleading result. It was believed that the surface chemical preparation was an essential step to have a relatively accurate CV reading. Our recent study, however, showed that the surface chemical preparation is not the only factor. The electrical charges on surface are equally important to the CV measurement. This work studied this effect on the Schottky CV measurements in detail. A new method has been developed in which an electrical surface preparation has been used prior to the CV measurement. The new method significantly improved the accuracy and repeatability of CV measurement.

MS-WeP2 A Two-Dimensional Modeling Study of Pattern Dependent Etching@footnote 1@*, B. Lay*, *M.J. Kushner,* University of Illinois, Urbana

Pattern dependent etching has become an increasingly important problem as feature sizes have decreased. It has been observed that a large exposed region on a die in close proximity to fine features tend to decrease the etch rates of the small features. In order to have process-independent uniform etching, the cause of this phenomenon must be determined. Previous studies have shown that gas phase processes alone, particularly at low pressures (< 10-20 mTorr), are unable to explain these observations. In this paper, the results of a numerical study of pattern dependent etching will be presented. A 2-dimensional computer model has been developed which addresses current flow through both the solid wafer material and the plasma. The Plasma-Solid-Simulator (PSS) solves Poisson's equation coupled with the continuity equations for electrons and ions in the plasma, and current density in the bulk, on a triangular mesh. The equations are linearized and implicitly integrated using Newton's method. The PSS calculates the conduction and displacement currents flowing through a partially exposed wafer during the etching process and relates them to etching characteristics. Parametric results from the PSS will be discussed as a function of plasma power and pattern layout. The observed increase in electric fields surrounding the unmasked portions of the wafer may lead to additional electron heating. @FootnoteText@ @footnote 1@This work was supported by SRC, AFOSR/DARPA, Applied Materials and LAM Research

MS-WeP3 Plasma Etch-Back Coupled to Chemical Mechanical Polishing for Sub 0.18 µm Shallow Trench Isolation Technology*, A. Schiltz,* France Telecom, CNET-CNS, France*; L. Palatini,* ESPEO - Orleans University, France*; M. Paoli, M. Rivoire, A. Prola,* France Telecom, CNET-CNS, FRANCE

This paper presents a new etch-back planarization technique with counter-masking to pre-planarize Shallow Trench Isolation substrates before Chemical Mechanical Polishing (CMP). A pre-planarization step is necessary since CMP alone cannot provide effective planarization for sub 0.18 technology due to dishing effect . The pre-planarization step uses the principle of Two Layer Planarization (TLP)@footnote 1@ technique which consists in spin-coating a first photoresist layer, using a counter-mask for the lithographic step, flowing and curing the resist blocks in STI topographies, spin-coating a second photoresist layer to planarize the residual topography and transferring the final flat surface into the substrate using plasma etch-back. In difference with previous techniques, we used a special mask with oversizing and exclusion of all STI critical dimensions smaller than 1.55 µm, the zones with the smaller STI dimensions being masked using a special narrow lines grid. Such a masking strategy avoids any misalignment problem, the resized first photoresist blocks are reflowed in STI topographies, leading to an easy planarization by the second resist layer. Additionally, the lithographic step is a non-critical step using conventional i-line resist. The final surface is transferred into the oxide substrate using (Ar/CF4/ O2) gas mixture in a LAM 4520 plasma etching equipment. To allow simultaneous etching of resist and oxide, various gas mixtures of Ar/x/O2 or Ar/x/y/O2 were tested, with x and y being chosen among following fluorine gas : CF4 - SF6 - C4F8 - CHF3. The (Ar/CF4/O2) gas mixture was observed to fulfill the etch back requirements with better performance. Equality of etch rate in resist and in oxide can be adjusted by the O2/CF4 gas ratio. A design of experiment (DOE) was used to determine the optimum conditions of plasma transfer of the planarized profile into the substrate. No ARDE (aspect ratio dependent etching) was observed, but loading effect was observed. Equality of etch rate in resist and in oxide during profile etch back transfer depends on oxide/resist surface ratio and therefore on the STI mask density. Then, equality of etch rate can be adjusted by the O2/CF4 gas ratio. Finally, the pre-planarized wafer is polished by CMP, resulting in an effectively planarized topography with residual topography smaller than 50 nm. The technique is a non-critical lithographic technique scaleable for technologies below 0.18 µm. @FootnoteText@ @footnote 1@ A. Schiltz and M. Pons, J. of the Electrochem. Soc., Vol. 133, 1, 178 (1986)

MS-WeP4 Composition of Si/Ge Films in Structures*, S. Soukane,* *T.S. Cale,* Rensselaer Polytechnic Institute*; C. Werner, A. Kersch,* Siemens, Germany*; M. Bloomfield,* Rensselaer Polytechnic Institute

In order to achieve optimum performance in SiGe base bipolar technology, the film composition must be carefully controlled.@footnote 1@ A detailed surface reaction mechanism for the chemical vapor deposition of SiGe on Si(100), using mixtures of hydrogen, dichlorosilane, hydrogen chloride and germane (H2, SiH2Cl2, HCl, GeH4) is discussed in this paper. The kinetic model involves a set of twelve reactions with several intermediate surface species, and includes both deposition and etching.@footnote 2@ Two reactions describe the migration of adsorbed chlorine and adsorbed hydrogen between silicon and germanium sites. Deposition simulations over device topographies are used to test the proposed kinetic model. Deposited film profiles, concentrations of each surface species, and composition (Si/Ge ratio) as a function of position in the simulated films, are predicted using the proposed chemical model in EVOLVE.@footnote 3@ We compare simulation results with available experimental data. @FootnoteText@ @footnote 1@1SiGeBase Bipolar Technology with 74 GHz fmax and 11 ps Gate Delay, T. F. Meister, H. Schafer, M. Franosch, W. Molzer, K. Aufinger, U. Scheler, C. Walz, M. Stolz , S. Boguth, and J. Bock, IEDM 95, IEEE, p.95-739 @footnote 2@2Kinetic Modeling of SiGe Deposition with SiH2Cl2 and GeH4, M. Hierlemann, C. Werner and H. Schafer, Abstract No. 726 in Electrochem. Soc. Abstracts Vol. 96-1, 1996, p. 900. @footnote 3@3EVOLVE is a low pressure transport and reaction simulator. EVOLVE 5.0b was released in November, 1998 (copyright T. S. Cale, 1989-1998).

MS-WeP5 Development of New Etching Algorithm for Ultra Large Scale Integrated Circuit and Application of ICP(Inductive Coupled Plasma) Etcher*, Y.-C. Lee,* *K.-R. Byun, S.-H. Park, J.-W. Kang, E.-S. Kang, O.-K. Kwon, H.-J. Hwang, T.-W. Kim,* Chung-Ang University, Korea

We proposed proper etching algorithm for ultra-large scale integrated circuit device and simulated etching process using the proposed algorithm in the case of inductive coupled plasma (ICP) source. Proposed algorithm calculates interactions both in plasma source region and in target material region, and uses binary collision approximation (BCA) method when ion impact on target material surface. Proposed algorithm considers the interaction between source ions in sheath region (from Quartz region to substrate region). After the collision between target and ion, reflected ion collides next projectile ion or sputtered atoms. In ICP etching, because the main mechanism is sputtering, both SiO2 and Si can be etched. Therefore, to obtain etching profiles, mask thickness and mask composition must be considered. Since we consider both SiO2 etching and Si etching, it is possible to predict the thickness of SiO2 for etching of ULSI. In this work, selectivity of Si and SiO2 is more than 50. The distribution of ions is calculated by Monte Carlo method and analytic model (plasma density 1012/cm3, pressures 1âˆ¼20mTorr), and the energy (ion flux corresponding to Maxwellian velocity distribution) increases by potential difference in sheath region. Projectile ion moves in time step, has direction and energy. When ion collides targets or ions, direction and energy is changed by impact parameter from binary collision approximation method. Proposed algorithm is efficient for computer calculation and easy to apply other cases. Results of etching simulation using proposed algorithm agree to results of SEM. In conclusion, in the case of ICP type reactor, proposed algorithm is appropriated to obtain etching profiles for ULSI process.

Nanometer-scale Science and Technology Division
Room 4C - Session NS-WeP

Poster Session

NS-WeP1 Tip Passive Chemical Modification and Its Effects on Tribological Measurements*, X.D. Xiao,* *L.M. Qian,* The Hong Kong University of Sci. & Tech., China

In this talk, we present our experimental results on the passive chemical modification process of the silicon nitride AFM tip by OTE/Mica, OTE/SiO@sub 2@, and SiO@sub 2@. The modified tips have different friction and adhesion properties against mica reference samples as compared to their pristine conditions. The resultant tip modification not only depends on the OTE SAM but also on the substrates the OTE SAM is prepared on. In the case of OTE/Mica, the friction of the modified tip against mica reference is much reduced; in the case of OTE/SiO@sub 2@, the friction of the modified tip against mica reference is much increased. It is surprising that bare SiO@sub 2@ can also chemical modify the Si@sub 3@N@sub 4@ tip to increase the friction against mica reference. In the case of OTE modification, it was found that the tips could be cleaned by repetitive friction scans on mica. However, tip modified by SiO@sub 2@ cannot be mechanical cleaned. Moreover, it was also found that humidity and load could also affect the tip chemical modification. Our results here is important for interpreting tribological data since the actual contact chemistry was often over-looked in the AFM experiments in the past.

NS-WeP2 Velocity Dependent Friction*, J.A. Heimberg, K.J. Wahl, I.L. Singer,* Naval Research Laboratory*; A. Erdemir, G. Fenske,* Argonne National Laboratory

Low friction, low wear diamond-like carbon (DLC)@footnote 1@ films have been studied under dry N@sub 2@ and dry air using a reciprocating tribometer. It was found that as the velocity decreased from mm's/sec to 10's µm/sec the friction coefficient dropped over an order of magnitude. The friction behavior was dependent on environment and counterface material. Tracks and balls have been analyzed for wear using optical and Raman microscopy. Conditions leading to the lowest friction will be discussed. The friction behavior can be quantitatively described in terms of gas adsorption models. @FootnoteText@ @footnote 1@ Work partially supported by the U.S. Department of Energy under Contract W-31-109-Eng-38. .

NS-WeP3 Gold Nano-wire Fabrication on Si(111) Using Piezoresistive Cantilevers*, T. Uchihashi, U. Ramsperger, H. Nejoh,* National Research Institute for Metals, Japan

Recent development of STM-based technology offers us unique opportunities to fabricate nano-scale structure in various ways in ultra-high vacuum (UHV). Although it is getting more and more established, measurement of electron conduction through nanostructures made in UHV has not been realized yet, except for scanning tunneling spectroscopy. Considering that there is a great demand for downsizing electronic circuit to nano-scale level, and that clean UHV condition is desirable to avoid surface contamination, such a measurement is highly demanded. Here, we present a novel but simple way of fabricating nano-scale metal wire on a clean substrate in UHV, which will enable us to realize such a measurement. As a gold-coated atomic force microscope (AFM) cantilever is brought into contact with a Si(111) sample surface, gold was transferred onto the sample surface, forming wires while the cantilever was moved laterally on the surface. Piezoresistive cantilevers (Piezolever,@footnote 1@ spring constant 2 - 10 N/m) were first coated with gold by thermal evaporation to a thickness of 50 to 60 nm. To fabricate gold wires on Si(111) surface, a gold-coated cantilever was brought into contact with sample surface and was moved laterally in a speed of 4 -32 nm/s. After this procedure, clear protruded line patterns were observed using STM. The minimum width of the lines was around 23 nm. In non-contact AFM mode, however, we found unusual line contrast change, according to the polarity of tip bias voltage. The probable reason for the line contrast change is charge transfer between silicon surface and gold. We also succeeded in connecting gold nano-wires to silver electrode pads, which was made by thermal evaporation in situ. The electrode pattern was defined by a through-hole mask, which was made of a titanium foil cut by focused ion beam. This demonstrates the possibility of measuring the properties of electron conduction through nanostructures made in UHV. @FootnoteText@ @footnote 1@ Courtesy of Park Scientific Instruments

NS-WeP4 Dual-Wavelength Scanning Near-Field Optical Microscopy*, P.R. LeBlanc, M. Gu, P. Grutter,* McGill University, Canada*; D. Gray,* PAPRICAN, Canada

We have developed a dual-wavelength Scanning Near-Field Optical Microscope to investigate biological samples in air. Using a helium-cadmium laser, we couple 442 nm and 325 nm light into a tapered optical fiber. Light transmitted through the sample is detected in a confocal arrangement. A dichroic mirror separates the two optical channels which are then detected by photomultipliers. The fiber tip is shaped, by immersion into a buffered hydrofluoric acid solution, to an aperture of less than 100nm and then coated with aluminum, defining a true sub-wavelength light source. Once coated, the tip is glued onto one of the tines of a quartz tuning fork which is then oscillated either parallel or perpendicular to the sample surface a few nanometers away. We have found that the latter method (gently tapping the surface) yields a resolution of greater than 20 nm topographical and 50 nm optical. An optical and topographical standard was created by lift-off of a 100 nm aluminum film evaporated on a close-packed monolayer of 500 nm diameter polystyrene spheres. Our initial focus for this instrument has been centered on the investigation of the lignin distribution in Black Spruce fibers. Lignin, a cross-linked phenolic polymer, is of paramount importance in the pulp and paper-making processes. It is a primary component of the wood cell wall and absorbs preferentially in the ultraviolet (it is the only component of the cell to do so). The dual-wavelength capability of our instrument permits the discrimination between chemical species density and topographical variations of the sample as well as near-field optical artifacts.

NS-WeP5 Influence of Secondary Tip Shape and Imaging Mode on Illumination Mode NSOM Images*, S.J. Stranick, C.E. Jordan, G.W. Bryant, R.R. Cavanagh, L.J. Richter,* National Institute of Standards and Technology

We report illumination-mode near-field optical microscopy images of individual 80-115 nm diameter Au particles with metal-coated fiber probes. It is found that the images are strongly influenced by the thickness of the metal coating. Theoretical models are presented which are in good agreement with the images. Wide probes with thick coatings (~lambda/2) produce images consisting of three extrema, due to a resonance-like polarization of the probe end. Narrow probes with thinner coatings produce wavy images, due to interference between the direct radiation from the tip and propagating tip fields scattered by the particles. Additionally, we have demonstrated a method for acquiring images that allows for the construction of three different imaging modes from one data set: constant-gap, constant-height, and constant-intensity. The method is based on the acquisition of topographic and optical data in a three-dimensional rather than a two-dimensional scanning format with controlled scans along the dimension normal to the surface. In this way, we acquire the topographic features of the sample surface as well as its optical response at various heights. This allows for the construction of constant-height and constant-gap images from the same data set and provides a means of identifying and correcting features that are a result of topographically induced optical contrast. Comparison between images recorded in this format to images 'lift-off' corrected by a single or small number of retraction curves indicates significant artifacts can still be present in corrected images.

NS-WeP6 InGaAs Quantum Dots fabricated by Separated-Phase Enhanced Epitaxy with Droplets (SPEED)*, T. Mano, K. Watanabe, S. Tsukamoto, Y. Imanaka, T. Takamasu,* National Research Institute for Metals, Japan*; H. Fujioka,* University of Tokyo, Japan*; G. Kido,* National Research Institute for Metals, Japan*; M. Oshima,* University of Tokyo, Japan*; N. Koguchi,* National Research Institute for Metals, Japan

Highly uniform InGaAs quantum dots (QDs) were successfully grown by Separated-Phase Enhanced Epitaxy with Droplets (SPEED) method. The SPEED is a novel method for self-organizing growth with highly dense Ga droplets produced by Droplet Epitaxy.@footnote 1@ All samples were grown on GaAs (001) substrates by molecular beam epitaxy method. After the growth of a GaAs buffer layer, an As-stabilized c(4x4) surface was formed as an initial surfaces. On this surface, 1.75ML of Ga, 2.5ML of In, and 50ML of Ga were supplied at 200°C, in order to compensate the 1.75ML excess As on c(4x4), to form the InGa droplets, and to form the highly dense Ga droplets surrounding the InGa droplets, respectively. After the formation of these droplets, which were very uniform in size, As flux was supplied at 200°C for crystallization and the sample was annealed at 500°C. At that time, the highly dense Ga droplets prevented the 2-dimensinal growth of the InGaAs and the separated-phase effect of InGaAs-GaAs was enhanced. Finally, a GaAs capping layer was grown. To confirm the effect of highly dense Ga, a reference sample was also fabricated with the same procedure except for the supply of 50ML Ga. In the case of the sample with the 50ML of Ga, not Stranski-Krastanov (S-K) mode but a flat surface is observed after the crystallization and annealing process. However, without 50ML of Ga, the S-K mode occurs. Although photoluminescence spectra of these samples are observed at same wavelength around 950 nm, the FWHM of the PL spectrum with 50ML Ga (22meV) is narrower than that of without 50ML Ga (100meV), and the intensity of PL spectrum with 50ML of Ga is thirty times stronger than that of without 50ML Ga. These results indicate that the uniform InGa droplets changed into the uniform InGaAs QDs embedded in GaAs. Therefore, the SPEED is very useful fabrication method for the high quality InGaAs QDs. @FootnoteText@ @footnote 1@ N. Koguchi and K. Ishige, Jpn. J. Appl. Phys. 32, 2057 (1993).

NS-WeP7 Diamond Growth from a Reconstructed Diamond(100) Monohydride in a Non-uniform Electric Field*, J.K. Kang,* Stanford University

We will present the effect of an electric field on the growth from a reconstructed diamond(100) monohydride with mechyl radical of CH3 with a growth species, which was examined at the ab initio density functional cluster calculation of the B3LYP theory. First of all, activation energies of various reaction steps involving in this growth under a non-uniform electric field, which is calculated using the electron orbital energies and vibration frequencies of these various reaction steps via the ab initio cluster calculation on cluster models, C9H14 and C38H40, will be compared to activation energies without an electric field. Finally, we will address that the non-uniform electric field can drastically change the surface reaction pathway by modifying the electronic structures and vibration frequencies, which corresponds to the modification of activation energies of various reaction steps involving in this growth.

NS-WeP8 Fabrication of a Nanosize Metal Aperture for NSOM Sensor using PR Removal and Sputtering Techniques*, M.Y. Jung, I.W. Lyo,* Yonsei University, Korea*; **S.S. Choi,*** Sun-Moon University, Korea

The scanning near-field optical microscopy(NSOM) can be used for imaging on a nanometer scale and identifying individual molecules with capability to surpass the resolution-limiting diffraction of conventional optical methods.@footnote 1@ In order to obtain better resolution limit, the diameter of the thin metal aperture has to be less than the optical wavelength. The fabricated nanosize Si tip using RIE have been thermally evaporated with a Au or Cr metal thin film. In order to have an aperture with diameter less than 100nm on top of the tip, several methods have been applied including sputtering and photoresist-stripping techniques.@footnote 2@ We have successfully fabricated the metal aperture with diameter less than ~0.3 nm on the silicon nitride tip. @FootnoteText@@footnote 1@ R.C. Davis, C.C. Williams and P. Neuzil, Appl. Phys. Lett. 66(1995) 2309. @footnote 2@M.Y. Jung, I.W. Lyo, S.S. Choi, MNE98, Sept.15-21, Leuven, Belgium. .

NS-WeP9 Non-destructive 1-D SCM Dopant Profiling Determination Method and Its Application to the 3-D Dopant Profiling*, **E.-S. Kang**, J.-W. Kang, H.-J. Hwang,* Chung-Ang University, Korea

As the scaling of feature size in the GSI device technology is continuing, the device characterization and life cycle is greatly affected due to an unexpected doping profile which is caused by 3-dimensional effects in mask corners and edges. Therefore, the experimentally determined 3-D impurity doping profile is needed to estimate these 3-D effects precisely. In this work, we present a new 1-D doping profiling determination method, which extends to the quantitative 3-D dopant profiling extraction. This is the non-destructive technique and method, which is different from conventional AFM/SCM measurement/dopant extraction and we can measure directly at real MOSFET device having 3-D structure. Through SCM modeling, we found the depletion layer in silicon was of a form of spherical capacitor with SCM tip biased. 2-D FDM (Finite Differential Method) code with SOR (Successive Over Relaxation) solver was developed to model the measurements by a SCM of a semiconductor wafer that contains an ion-implanted impurity region. And we analyzed this capacitor theoretically and determined the depleted total volume charge (Q), capacitance (C) and the rate of capacitance change with bias (dC/dV). It is very important to observe the depleted carriers movement in the silicon layer by applying a bias to tip. So we calculated the depleted volume charge considering some factors such as tip size, oxide thickness and applied bias (dc + ac) which has effect on the potential and depletion charge. Finally, we developed 1-D inversion algorithm to convert SCM measurement output (dC/dV) into real dopant concentration, comparing SCM signal output with the calculated dC/dV through SCM modeling. We assume 1-D Pearson distribution function having several parameters as the initial profile. This profile extraction procedures consist of finding the profile that minimizes the least squares fit criterion between the calculated dC/dV and the measured dC/dV.

Topical Conference on Emerging Opportunities and Issues in Nanotubes and Nanoelectronics
Room 4C - Session NT+NS+EM+MS-WeP
Poster Session

NT+NS+EM+MS-WeP1 Growth of Carbon Nanotubes at Low Temperature by Microwave Plasma-enhanced Chemical Vapor Deposition*, **Y.C. Choi**, D.J. Bae, Y.H. Lee, B.S. Lee,* Jeonbuk National University, Korea

We have grown carbon nanotubes at temperatures below 520 C by microwave plasma-enhanced chemical vapor deposition using methane and hydrogen gases. Carbon nanotubes were uniformly grown in large area of transition metal-coated Si substrates with high density. Each nanotube is terminated by transition metal cap, suggesting that the transition metals play an important role in the nanotube growth. Carbon nanotubes are curly in all cases, indicating the nanotubes to be defective due to very low growth temperature. Diameters and lengths of the nanotubes could be controlled by changing the ratio of methane to hydrogen and growth time. Raman spectum clearly shows the peak at 1592 cm-1 (G-band), indicating the formation of well graphitized carbon nanotubes.

NT+NS+EM+MS-WeP2 Nanoscale-controlled Handling of Carbon Nanotubes*, **O. Jaschinski**, P. Bernier, L. Vaccarini, C. Goze,* Universite Montpellier II, France*; G. Duesberg,* Trinity College Dublin, Ireland*; C. Journet, S. Roth,* Max-Planck-Institut fuer Festkoerperforschung Stuttgart, Germany

Carbon nanotubes are the most promising materials for applications in nanoelectronics and nanomechanics. For the determination of the electrical and mechanical properties of nanotubes and for the production of nanotube devices one needs the ability to handle nanoscale materials in a controlled way . We demonstrate how atomic force microscopy (AFM) can be used as a tool for manipulating and investigating carbon nanotubes. For an optimal use of AFM it is necessary to control the substrate-nanotube interaction. We present results of measurements of the mechanical properties of nanotubes obtained with various kinds of substrates. We show how the combination of lithography, manipulation by AFM and control of the adsorption process of nanotubes allow to prepare well defined sample configurations for very sophisticated measurements of the electrical and mechanical properties of carbon nanotubes. Based on these methods, techniques for the production of nanotube devices can be developed. This work was supported by European TMR contract NAMITECH ERBFMRX-CT96-0067 (DG12-MIHT)

NT+NS+EM+MS-WeP3 Aligned Carbon Nanotubes with Controlled Diameters Using Anodic Alumina Template*, **S.-H. Tsai**, H.C. Shih,* National Tsing Hua University, R.O.C.

The microwave plasma enhanced chemical vapor deposition (MPECVD) system had been successfully fabricated the well-controlled diameters of aligned carbon nanotubes on the anodic alumina template with a mixture of methane and hydrogen. Prier to test, the anodic alumina with pore arrays in various diameters were prepared by anodizing aluminum using oxalic, sulfuric, and phosphoric acid solutions. By adjusting the pore size of the anodic alumina, various carbon nanotube diameters can be obtained in a range of 30 to 100 nm and were examined by scanning electron microscopy and transmission electron microscopy.

NT+NS+EM+MS-WeP4 The Selective Growth of Aligned Carbon Nanotubes by PECVD Using Nickel Catalyst*, **H. Jeon**, K. Ryu, M. Kang,* Hanyang University, Korea

Carbon nanotubes have been studied extensively because of their own unique physical properties and also of their application potential for field emitters. One of the interesting applications is reported for display application, but neither industrial fabrication technology nor performance has been reported for practical display application. Here we tried to grow aligned carbon nanotubes selectively by plasma enhanced chemical vapor deposition (PECVD) method using nickel catalyst@footnote 1@ at temperatures below 600°C. These conditions for low temperature growths are suitable for field emission display which requires carbon nanotube emitters grown perpendicular to the Si substrate. In our experiment, a thin film of nickel(10-100nm) was deposited through a pattern mask on a Si substrate in UHV e-beam evaporator and was agglomerated by in-situ annealing for thirty minutes at 700°C. The use of a patterned catalyst enhanced the formation of selectively aligned nanotubes at low temperatures. After this process, Ni particles deposited on Si substrate were examined by AFM and SEM. Carbon nanotubes were selectively grown on Ni particle by PECVD with using the mixture of CH@sub 4@ and NH@sub 3@ at 600°C. In this process, CH@sub 4@ was used as the carbon source and NH@sub 3@ was used as a catalyst and dilution gas. During the process, many carboneous impurities can be produced and tried to eliminated by introducing H@sub 2@ plasmas. We examined the physical properties of carbon nanotubes by SEM, XRD and Raman spectroscopy. And we investigated the formation temperature of carbon nanotubes on silicon substrate and controlled the selective growth of aligned nanotubes. @FootnoteText@ @footnote 1@ Masako Yudasaka, et al.,Appl. Phys. Lett. 70(14), 7 April 1997.

Surface Science Division
Room 4C - Session SS-WeP
Poster Session

SS-WeP1 Strain and Strain Relief in Gadolinium(0001) Thin Films on Mo(112)*, **T. Komesu**, H. Jeong, P.A. Dowben,* University of Nebraska, Lincoln

The electronic structure of strained and unstrained Gd(0001) has been studied with spin-polarized photoemission spectroscopy and spin-polarized inverse photoemission spectroscopy. In this work, we observed that relaxation of the expansively strained crystal in-plane lattice constant, of Gd(0001) on Mo(112), significantly diminishes the differences in the electronic structure from that observed for Gd(0001) grown on W(110). The defects incorporated in Gd films, with increasing film thickness, lead to both lattice relaxation and a loss of net polarization for Gd(0001) grown on Mo(112).

SS-WeP2 Formation process of a Cu-Zn surface alloy on Cu(111) investigated by STM*, M. Sano*, *S. Ishikura,* University of Tsukuba, Japan*; T. Fujitani,* National Institute for Resources and Environment, Japan*; J. Nakamura,* University of Tsukuba, Japan

We had previously shown that a Zn-deposited Cu(111) surface is a good model for methanol synthesis by the hydrogenation of CO@sub 2@, and a Cu-Zn surface alloy is active species for the reaction. Here, we investigated the formation process of the Cu-Zn surface alloy formed on a Zn-deposited Cu(111) surface by STM. The STM measurements were carried out using a UHV-STM apparatus equipped with LEED-AES. Zinc was deposited on Cu(111) by resistively heating a Zn wire. STM image of the surface after the Zn deposition at room temperature showed that the bright atoms were localized in the vicinity of step edges. These blight atoms were considered as Zn atoms substituted for the substrate Cu atoms. The density of Zn atoms decreased with increasing distance from step edges and no Zn atoms were observed on the terrace away from the steps. The migration of Zn atoms over the surface was observed by time resolved STM measurements. The migration rate was determined to be 6.67x10@super -3@ s@super -1@ and the mean residence time was 150 s. These results indicate that the alloying initially occurs around steps and then Zn atoms migrate over the terrace. On the other hand, after annealing the Zn-deposited Cu(111) at 523 K, STM images showed that Zn atoms were distributed homogeneously over the Cu(111) surface. The Zn coverage estimated by the STM images was in good agreement with that measured by AES. Pair-correlation analysis of the NN distribution for Zn atoms suggested that Zn atoms were randomly distributed on the terraces, indicating that Zn atoms were randomly substituted for Cu atoms leading to the Cu-Zn surface alloy.

SS-WeP3 Microkinetics of Formate Synthesis on Cu Catalysts*, T. Fujitani,* National Institute for Resources and Environment, Japan*; I. Nakamura, H. Nishimura, H. Nakano, J. Nakamura,* University of Tsukuba, Japan

The kinetics of formate synthesis by hydrogenation of CO@sub 2@ and formate decomposition has been studied on Cu(111) and Cu(110) surfaces using in-situ IRAS and STM apparatuses combined with a reactor (1 atm). It has been found that the formate synthesis does not depend on the surface structure of copper between Cu(111) and Cu(110). The activation energy of formate synthesis on Cu(111) and Cu(110) have been determined to be 68.3 and 69.7 kJ/mol, respectively. The microkinetics of the formate synthesis can be explained by that assuming an Eley-Rideal mechanism. On the other hand, the activation energy and the pre-exponential factor for formate decomposition on Cu(111) were different from those on Cu(110), indicating that the decomposition of formate species depend on the Cu surface structure. Furthermore, the decomposition rate of formate on Cu(111) is very different depending on the preparation method, the synthesis from CO@sub 2@ and H@sub 2@ at atmospheric pressure and the preparation by adsorption of HCOOH in UHV. However, the activation energy of the decomposition for both cases is close to each other, meaning that the frequency factor of the rate constant is different for the two cases. The difference can be explained by the different structures of formate observed by STM. In the presence of atomic hydrogen, the decomposition rate of the formate synthesized from CO@sub 2@ and H@sub 2@ increases and becomes equal to the decomposition rate of the formate prepared by the adsorption of HCOOH. The activation energies and the pre-exponential factors for both the formate synthesis and the formate decomposition on Cu/SiO@sub 2@ were in good agreement with those on Cu(111), suggesting that the surface structure of Cu for the Cu/SiO@sub 2@ catalyst is identical with the Cu(111) surface.

SS-WeP4 The Adsorption-Desorption Properties of CO on W(111) Surface*, S.-B. Lee,* *S.-Y. Lee, Y.-D. Kim, T.S. Yang, J.-H. Boo, C.Y. Park,* SungKyunKwan University, Korea*; H.-T. Kwak,* Kook Min University, Korea

The adsorption and desorption properties of CO have been studied on W(111) surface in the temperature range of 300 - 1100 K by LEED, XPS, UPS, and TDS. After CO saturation at 300 K, four adsorption states obtained from TDS experiment were observed at 400, 850, 1000, and 1100 K, called @alpha@, @beta@@sub 1@, @beta@@sub 2@, and @beta@@sub 3@ states, respectively. The desorption temperature of @beta@@sub 3@-CO state shifted to higher temperature with increasing CO exposure signifying an attractive lateral interaction between adsorbed species. Using Bragg-Williams approximation the lateral interaction energy (-5.7 kJ/mol) was calculated and the TD-spectra obtained experimentally were successfully simulated using by quasi-chemical approximation. The desorption kinetic order of the @beta@@sub 3@-CO state is followed by the first order indicating that the adsorbed state of @beta@@sub 3@-CO seems to be a molecular state rather than that of dissociated state. With UPS and XPS, the CO adsorption property (especially the @beta@@sub 3@-CO) on W(111) was clearly confirmed. The adsorption of CO on W(111) at 300 K exhibited only one emission peak at -6.3 eV below Fermi level due to 1@pi@+5@sigma@ molecular orbitals of CO. With heating the adsorbed CO to 1000 K, however, an additional emission peak was also observed at -7.1 eV due to an orbital energy splitting of 1@pi@+5@sigma@. This is strongly supported with a theoretical result calculated by ASED-MO method. Comparing the O state of @beta@@sub 3@-CO with that obtained from the dissociatively adsorbed oxygen species, we can identify that the @beta@@sub 3@-CO is different with that for dissociated CO suggesting a non-dissociated CO species with different geometry. From these results, a lying-down species of adsorbed CO is proposed.

SS-WeP5 Ordered Structures of Oxo Overlayer on Cu(111) Electrode Surface in an Alkaline Electrolyte Revealed by Electrochemical STM*, O. Matsuoka*, *S. Yamamoto, S. Sugiyama,* Mitsui Chemicals, Inc., Japan*; H. Nozoye,* National Institute of Materials and Chemical Research, Japan

Redox behavior of copper surface in aqueous solution is of great interest in many industrial fields, such as energy, catalytic, and microelectronic applications. Many characterization studies on copper electrode surface revealed that surface oxygen is not entirely removed even at the potential corresponding to the onset of hydrogen evolution. This oxo overlayer on surface is considered active for catalytic reactions.@footnote 1@ Information about the structure and behavior of oxo overlayer in aqueous solutions seems to provide a proper understanding of reacting mechanism of copper catalysts. We have investigated the structure of Cu(111) electrode surface that have an oxo overlayer in an 0.01M NaOH aqueous solution by using electrochemical scanning tunneling microscope (EC-STM). Two kinds of periodical structures of bright spots were observed.@footnote 2@ Dimensions of these periodical structures were similar to the unit cell for the (@sr@7 x @sr@7) and (2@sr@7 x 2@sr@7). The periodical structure similar to (@sr@7 x @sr@7) appeared at a cathodic wave at -0.9 V vs. Ag/AgCl on cyclic voltammogram, and this periodical structure was converted into (2@sr@7 x 2@sr@7) at more negative potential. Anodic wave related with the cathodic wave at -0.9 V appeared in anodic sweep. The potential of this anodic wave was different between these two periodical structures. We consider these periodical structures show an alignment of CuOH surface species which created by the reduction of sub-surface oxygen.@footnote 3@ @FootnoteText@ @footnote 1@L.D.Burk, et al., J.Electrochem.Soc., 137,553(1990) @footnote 2@O.Matsuoka, et al., Chem.Lett., 947(1998) @footnote 3@S.Haetinger, et al., J.Electroanal.Chem., 397,335(1995).

SS-WeP6 Structure of MnO@sub x@/Rh(100) studied by STM*, H. Nishimura*, *T. Tashiro,* University of Tsukuba, Japan*; T. Fujitani,* National Institute for Resources and Environment, Japan*; J. Nakamura,* University of Tsukuba, Japan

A modified Rh/SiO@sub 2@ catalyst with Fe or Mn shows excellent catalytic activity for the hydrogenation of CO into C@sub 2@ oxygenates such as acetic acid, ethanol and acetoaldehyde. The active sites may be located at the interface between Rh and MnO@sub x@ species. We have studied the structure of a MnO@sub x@ deposited Rh(100) surface using an ultra high vacuum scanning tunneling microscope (UHV-STM). The deposition of Mn over a Rh(100) surface was performed by resistively heating a Ta boat and then the Rh sample was annealed in an oxygen atmosphere to prepare the MnO@sub x@ species. The STM images showed a c(2x2) structure and a characteristic square unit (30 Å x 30 Å), which were tentatively assigned to Mn-Rh surface alloy and MnO@sub x@ species, respectively. A (111) like structure with six-fold symmetry was also assigned to MnO@sub x@ species.

SS-WeP7 Electrochemical Scanning Tunneling Microscopy of Copper Adlayers on Iodine-Covered Au(111) in Sulfuric Acid Solution, *A. Martinez-Ruiz,* CICESE & Fac. de Ciencias, UABC, MEXICO*;* ***J. Valenzuela-Benavides****, L. Morales de la Garza,* CCMC-UNAM, Mexico*; N. Batina,* UAM-Iztapalapa, Mexico*; F. Castillon,* CCMC-UNAM, Mexico

We present structural and electrochemical studies of copper electrodeposition on the Au(111) surface precovered with iodine in a sulfuric acid solution. In situ electrochemical scanning tunneling microscopy (STM) studies reveal different adlayer structures depending on the potential of the gold working electrode. Before initiating the underpotential deposition (UPD) of copper, a (5x@sr@3) structure of the iodine adlayer is observed on wide terraces as reported in a similar study with perchloric acid solution. For more negative potentials, the (5x@sr@3) structure transforms to a (3x3) structure around 320mV (vs a Cu/Cu@super ++@ electrode). Cyclic voltammetry (CV) suggests that not enough copper is depositing at this potential to cause the observed (3x3) structure to form, since only a significant ammount of copper deposition begins at potentials below 250mV. This is in sharp contrast to the reported study performed in perchloric acid solution, where the (3x3) is attributed to the UPD of copper of approximately less than half of a monolayer. At the end of the UPD process a (@sr@3x@sr@3)R30@super o@ structure is observed. All these structures are also observed during the CV anodic cycle, returning to the initial (5x@sr@3) structure of the iodine adlayer, which can be removed at a more positive potential with the iodine atoms diffusing into the solution, leaving a bare Au(111) surface. The above results strongly indicate that the stable iodine layer exist on the top layers of Cu and Au during deposition and stripping of Cu. The presence of anions is discussed which may explain the difference between the CV data and the STM images.

SS-WeP8 Lateral Compression of a Xe Film Physisorbed on the Surface of a Silver Single Crystal*, S. Igarashi*, *A. Tosaka, T. Hirayama, I. Arakawa,* Gakushuin University, Japan

The layering transition of a physisorption system on a metal single crystal has been investigated by means of an ellipsometry and an eXtremely-low-current LEED (XLEED). Our XLEED system is operated at the primary electron current of about 1 pA or less, which minimizes the effect of desorption, defect formation, and charging.@footnote 1@ We observed the surface structure of Xe/Ag(111) by XLEED while monitoring the layer growth by the ellipsometry from a submonolayer film to a thick one. An equilibrium between the Xe film and coexisting three-dimensional Xe gas has been maintained throughout the experiment. From a monolayer film to a sufficiently thick film, the Xe overlayer has clear hexagonal structure whose directions of the unit vectors are coincident with those of the substrate. The Xe-Xe spacing in the monolayer film on Ag(111) is known to be a few per cent larger than that of bulk. Our interest is how the Xe-Xe spacing varies in the process of layer growth. We have made a systematic observation of the change of the Xe-Xe spacing in one and two monolayer films at pressures between 10@super -7@ and 10@super -2@ Pa and at temperatures between 50 and 100 K. In the case of isothermal growth at 78.4 K, for example, the Xe-Xe spacing of the monolayer film is 4.53 Å at immediately after the first layer condensation at 1x10@super -5@ Pa and decreases gradually to 4.5 Å with increasing a surrounding pressure up to 1x10@super -3@ Pa. Then the spacing decreases rapidly and reaches almost that of bulk, 4.39 Å, just before the second layer condensation at the pressure of 4x10@super -2@ Pa. @FootnoteText@ @footnote 1@ S. Igarashi, Y. Abe, Y. Irie, T. Hirayama and I. Arakawa, J. Vac. Sci. Technol. A 16, 974 (1998).

SS-WeP9 A Comparative Study for Small Molecule Adsorption onto Stoichiometric and Defective TiO@sub 2@ and SrTiO@sub 3@ Surfaces*, K.F. Ferris*, *L. Wang,* Pacific Northwest National Laboratories

Interactions of water and HCOOH with stoichiometric and defective TiO@sub 2@(100), TiO@sub 2@(110), and SrTiO@sub 3@(100) surfaces have been studied using electronic structure calculations. This paper presents a comparative study for the relationship between adsorbate interactions and reactivity focusing on the role of surface structure. Preliminary results for formate interaction with SrTiO@sub 3@(100) indicate strong adsorption consistent with experimental results, but in a distinctly different geometric arrangement due to absence of bridging oxygens present for the TiO@sub 2@ surfaces. This absence directly affects the water adsorption and dissociation behavior for SrTiO@sub 3@. Structural differences again modulate the reactivity of defect sites. Further results will be discussed in terms of potential reaction mechanisms and correlations with ongoing experimental studies.

SS-WeP11 Structural and Chemical Investigations on Different Polar ZnO Surfaces*, St. Hoevel*, *Th. Beker, Ch. Boas, U. Burghaus, K. Weiss, M. Wuehn, C. Kolczewski, V. Staemmler, Ch. Woell,* Ruhr-Universität Bochum, Germany

We report on investigations of the structural and chemical properties of the two differently terminated Zn(0001) surfaces. The clean, oxygen terminated surface was studied with helium atom scattering (HAS) and LEED. The peak-shapes of the He-atom diffraction peaks and the variation of the He-atom reflectivity as a function of He-atom wavelength provide detailed information on the surface morphology (step height distribution, average terrace width, type of defects). As regards the chemical properties of the surface (e.g. presence of acidic sites), we studied the adsorption behaviour of pyridine on the two differently terminated ZnO(0001) surfaces with thermal desorption spectroscopy (TDS), x-ray photoelectron spectroscopy (XPS), and x-ray absorption spectroscopy (NEXAFS). The interpretation of the latter results is based on precise ab-initio electronic structure calculations for a model compound. The binding energy of pyridine on the O-terminated (000-1)-surface amounts to 57 kJ/mol and the spectroscopic data reveal only small modifications of the pyridine electronic structure, indicating the presence of a physisorbed species. On the Zn-terminated ZnO(0001)-surface the binding is substantially stronger, 112 kJ/mol, and the N1s NEXAFS-data for the pyridine @pi@*-resonance shows a shift of 0.6 eV towards higher binding energies. This observation indicates a substantial interaction between the nitrogen lone pair and the Zn d electrons, as confirmed by the ab-initio calculations.

SS-WeP12 Formation of a Smooth and Pure Chromium Oxide Film on Stainless Steel Surface by Oxidation*, B. Cho*, *S. Chung,* Pohang University of Science and Technology, South Korea

Oxidation of stainless-steel for annealing temperature of 450 °C in oxygen partial pressures of 10@super -9@ to 10@super -4@ Torr was tested to form a smooth and pure chromium oxide film on the surface. Atomic force microscopy and scanning tunneling microscopy images show that oxidations in low oxygen pressures (10@super -9@ and 10@super -8@ Torr) favor the formation of not only macroscopically but also atomically smooth oxide films, which is almost total chromium oxide, as characterized by X-ray photoelectron spectroscopy. But oxidations in high oxygen pressures (10@super -6@ and 10@super -4@ Torr) prefer the development of very rough oxide films with distinct grains and significant proportion of iron. Considering that rough surfaces usually provide more adsorption sites for impinging molecules than smooth surfaces and pure chromium oxide films block hydrogen diffusion from bulk material more efficiently than inhomogeneous iron-rich oxide films, oxidation with low oxygen pressure may be a promising technique for the fabrication of a stainless steel vacuum chamber with enhanced outgassing characteristics.

SS-WeP13 The Interaction of Water with the Basal Plane of @alpha@-Cr@sub 2@O@sub 3@: Dissociation and Multiply Coordinated Adsorption Sites*, M.A. Henderson*, *S.A. Chambers, C.L. Perkins,* Pacific Northwest National Laboratory

We have examined the interaction of water with an @alpha@-Cr@sub 2@O@sub 3@(001) thin film surface using TPD, HREELS and LEED. The @alpha@-Cr@sub 2@O@sub 3@(001) film is the terminus of an alternating @alpha@-Cr@sub 2@O@sub 3@/@alpha@-Fe@sub 2@O@sub 3@ heterostructure grown on an @alpha@-Al@sub 2@O@sub 3@(001) substrate using molecular beam epitaxy. The @alpha@-Cr@sub 2@O@sub 3@ lattice is 2@super o@ expanded inplane due to lattice matching to the @alpha@-Fe@sub 2@O@sub 3@. Water interacts strongly with the @alpha@-Cr@sub 2@O@sub 3@(001) surface, desorbing in two prominent TPD states at 345 and 297 K, both of which exhibit first-order desorption behavior. Weaker binding TPD states are observed at 210 and 185 K. Using a calibrated doser, TPD results indicate that the coverage of water in the 345 and 297 K TPD states is twice that of the surface Cr@super 3+@ coverage suggesting that each surface cation site binds two water molecules. Although no irreversible decomposition is detected by TPD, HREELS (acquired at room temperature to avoid sample charging) shows prominent losses at 3605, 2890 and 915 cm@super -1@. Using D2O, the latter two losses shift to 2645 and 2135 cm@super -1@ and the former is undetected (shifted under the lattice phonon modes). The 3605/2645 cm@super -1@ and 915/(?) cm@super -1@ losses are indicative of the hydroxyl stretching and bending modes, respectively, of a terminal hydroxyl group, whereas the 2890/2135 cm@super -1@ losses are suggestive of a very weak hydrogen-bonding interaction, probably between the deposited hydrogen/deuterium atom and the terminal OH/OD group. Although this hydrogen-bond is weak, as suggested by its low O-H stretching frequency, the dynamic dipole of its O-H stretch is as strong as that of the terminal OH group. Although HREELS analysis of the 297 K TPD state is in progress, our tentitive model is that each surface Cr@super 3+@ site binds both a molecular and dissociative form of water. The absence of strong coverage dependence in the TPD suggests that these water species are only weakly interacting. The role of lattice expansion will also be discussed, in comparison with studies on an unstrained @alpha@-Cr@sub 2@O@sub 3@(001) film (to be conducted).@footnote 1@ @FootnoteText@ @footnote 1@ This work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of

Materials Sciences. Pacific Northwest National Laboratory is a multiprogram national laboratory operated for the U.S. Department of Energy by Battelle Memorial Institute under Contract DE-AC06-76RLO 1830. The research reported here was performed in the William R. Wiley Environmental Molecular Science Laboratory, a Department of Energy user facility funded by the Office of Biological and Environmental Research.

SS-WeP14 In-situ Study on the Formation of SiC Thin Films on Si(111) Surface with 1,3-disilabutane: Adsorption Properties and Initial Deposition Characteristics*, H.G. Yoon, J.-H. Boo, S.-B. Lee,* ***W.L. Liu,*** SungKyunKwan University, Korea*; S.-C. Park, H. Kang,* Pohang University of Science and Technology, Korea*; Y. Kim,* Korea Research Institute of Chemical Technology, Korea

The adsorption properties of 1,3-disilabutane (DSB), SiH@sub 3@-CH@sub 2@-SiH@sub 2@-CH@sub 3@, and an initial deposition characteristics for the formation of SiC thin films on Si(111) surfaces have been studied in the temperature range of 150 - 1200 K in situ by XPS, UPS, TDS, and Cs@super +@ ion reactive scattering methods. After DSB dosing at 300 K, only one adsorbed state was obtained from XPS and UPS. The C 1s and Si 2p XP spectra appeared at ca. 283 and 99.5 eV showed no chemical (binding energy) shifts between RT and 600 K indicating a SiC cluster and/or islands formation. With increasing the surface temperature to 1200 K, however, a gradual binding energy shifts of both Si 2p and C 1s XP peaks to the higher values were observed due to a crystalline SiC thin film deposition. During deposition, moreover, we also identify the intermediate states of the thermal decomposition reaction of DSB on a Si(111) surface with Cs@super +@ ion reactive scattering. Several kinds of intermediates as CsCH@sub 4@Si@super +@, CsC@sub 2@H@sub 8@Si @sub 2@@super +@, CH@sub 4@Si@super +@, and CH@sub 3@Si@super +@ were detected at 150 K. In the case of DSB deposition between 800 K and 950 K, on the other hand, only one intermediate (i.e. CsCH@sub 4@Si@super +@) was observed indicating that most of C@sub 2@H@sub 8@Si@sub 2@ adsorbates have been reacted away at these temperatures, forming either CH@sub 4@Si or SiC thin films on the surface. Based on the experimental results of XPS, UPS, TDS, and Cs@super +@ ion reactive scattering, in this work, we proposed a possible chemisorption geometry and decomposition mechanism of DSB.

SS-WeP15 Real-time VT-STM Studies of Dewetting Processes: Ag/Si(111)*,* ***K. Th@um u@rmer****, E.D. Williams, J.E. Reutt-Robey,* University of Maryland

Under typical MBE-conditions thin film morphology is often limited by kinetics. An excellent model system for film growth proceeding far from equilibrium is silver, deposited at room temperature on Si(111) (see review@footnote1@). At a mean film thickness of 1nm, the substrate is completely covered by worm-like structures. Using a variable temperature STM, we have studied the transformation of these metastable structures into equilibrium shaped hexagonal crystallites. By tracking the annealing process in real time, we encounter an astonishing variety of transition shapes. At ~200C the onset of de-wetting exposes substrate areas with a root3 x root3 reconstruction. The higher mobility on these denuded areas acts as a positive feedback, accelerating the decay of adjacent structures. At ~300 C the morphology is dominated by 500 nm wide and 100 nm high crystallites, exhibiting networks of partial dislocations on their (111)-top facets. This work has been supported by the NSF-MRSEC at University of Maryland under grant #DMR-96-32521. @FootnoteText@ @footnote 1@ H.Neddermeyer, Critical Rev. in Solid State and Material Science 16(5),309 (1990) 29, 30, 53-55, 57, 68.

SS-WeP16 Dissociative Reaction of HBO@sub 2@ Molecules on Si(111)-7x7 Surface Studied by Scanning Tunneling Microscopy*,* ***K. Miyake****, T. Kaikoh, Y.J. Li, H. Shigekawa,* University of Tsukuba, Japan

Boron (B) has been attracting considerable attention as a promising c andidate for the formation of atomic-layer doped structure. Atomic-layer dop ing process on Si substrate consists of two parts; adsorption of a monolayer fraction of dopant atoms on Si surface and subsequent Si growth. Therefore, precise control of B atoms on Si surface is essentially important. Recently, HBO@sub 2@ molecules were found as a most appropriate boron source because o f its higher vapor pressure compared to the metal boron cases. However, how HBO@sub 2@ molecules react with the Si surface still remains as an open ques tion. In order to clarify this point, we characterized the chemical reaction process of HBO@sub 2@ molecules on Si(111)-7x7 surface in detail. We succeed ed in confirming two different states of HBO@sub 2@ molecules on the surface . When the substrate temperature during HBO@sub 2@ irradiation was kept at 3 00°C, the adsorbed HBO@sub 2@ molecules remained on the surface witho ut dissociation. On the other hand, when the substrate temperature was kept at 600°C, HBO@sub 2@ molecules were dissociated, and the oxygen- and boron-related adatoms were produced at corner and center adatom sites in 7x7 units, respectively. Taking the difference in the electronegativity between the oxygen and boron atoms into consideration, oxygen and boron atoms in HBO @sub 2@ molecules are expected to react with adatoms and rest atoms, respect ively. Then, as a result of the dissociation of HBO@sub 2@ molecules, oxygen and boron atoms may adsorb at the corner and center adatom sites, respective ly. In order to confirm this reaction process, the sample formed by HBO@sub 2@ irradiation at 300°C was annealed at 600°C for 1min. As exp ected, non-reacted HBO@sub 2@ molecules disappeared and the oxygen- and boro n-related adatoms were observed after annealing. These results indicate high controllability of chemical reaction process of HBO@sub 2@ molecules on Si(1 11)-7x7, and high potential exists in this system. @FootnoteText@ http://dora.ims.tsukuba.ac.jp

SS-WeP17 Investigation of Sulfur-terminated GaAs(001) Surfaces by Selective Atoms Sublimed Method*,* ***S. Tsukamoto****, T. Ohno, N. Koguchi,* National Research Institute for Metals, Japan

Recently, a novel S-termination method has been developed by exposure to S vapor in molecular beam epitaxy system, observing not diffused (2x1), commonly reported, but clear (2x6) reconstruction by reflection high-energy electron diffraction and scanning tunneling microscopy(STM).@footnote 1@ Then, we found that the separations, 0.19 - 0.28 nm, between S atoms of S dimers by STM well agreed with the first-principles pseudopotential calculated result, 0.237nm, with the condition of one electron transferred from each S dimer.@footnote 2@ However, the (2x6) structure is still not clear. In this paper, we study the detail of this (2x6) by the investigation of the structural change by a selective atoms sublimed method which uses the thermal desorption of selective S-S dimer from the (2x6). The calculated maps of the charge-density contours of the S-S structures show that the center of the charge-density is as same as the poison of the S atom in the case with the transfer of one electron. On the other hand, in the case without the transfer, the center of the charge-density is about 0.05nm far from the position of the S atom. Therefore, if the charge-density balance is destroied by the thermal desorption, the observed S-S bond length by STM will be drastically changed. The (2x6) structure turns into the (2x3) structure at around 520°C releasing about 20% surface sulfur atoms, which amount consist with the central dimer pairs of the (2x6) structure, however, without interdiffussion and with keeping the same S-S bond length. In addition, the Ga small clusters appeared on this (2x3) surface. It seems that these Ga clusters kept the charge-density balance of the (2x3) structure, keeping the same S-S bond length. @FootnoteText@ @footnote 1@S.Tsukamoto and N.Koguchi, Jpn.J.Appl.Phys., 33 (1994) L1185; Appl.Phys.Lett., 65 (1994) 2199; J.Cryst.Growth., 150 (1995) 33. @footnote 2@S.Tsukamoto, T.Ohno, and N.Koguchi, J.Cryst.Growth., 175/176 (1997) 1303.

SS-WeP18 Dynamical Behavior of Hydrogen Molecule on GaAs(001) Surface*,* ***M. Ohashi****, M. Ozeki, J. Cui,* JRCAT - ATP, Japan

Hydrogen plays important roles as an important reactant and a carrier gas in various surface processes of III-V compound semiconductors. However there are no sufficient data on dynamical behaviors of hydrogen on III-V compounds surface. Supersonic molecular-beam scattering enables us to bring valuable dynamical parameters such as reaction probability, reaction pathway, reaction kinetics, and activation energies of reaction steps. We have been studying in dynamical behaviors of hydrogen on GaAs(001) surface by supersonic molecular beam apparatus. We measured angular distributions of reflected beams, when hydrogen molecule was injected with 110 and -110 directions onto GaAs(001) 2x4 surface. The existence of trapping/desorption channel was clearly discovered and the depth of potential well of hydrogen molecule on GaAs(001) 2x4 surface was estimated 0.4 kcal/mol by the trajectory simulation of trapping probabilities. The angular distribution of reflected hydrogen molecule of trapping/desorption channels direct scattering was largely affected by the surface corrugation of GaAs(001) 2x4 surface. The experimental result was compared by classical trajectory simulation for this system. The experimental result agreed excellently with classical trajectory simulation. This indicated the important information of the energy exchange from translational to rotational modes was indicated. This work is supported by New Energy and Industrial Technology Development Organization (NEDO).

SS-WeP19 Study on Properties of Defects and Boron at the Si/SiO@sub 2@ Interface using Empirical Interatomic Potential Energy Function*, J.-W. Kang, H.-J. Hwang,* Chung-Ang University, Korea

Properties of silicon/oxide interface were computed using novel interatomic potential-energy function that was recently developed@footnote 1@ for modeling the interactions between silicon and oxygen atoms. For boron-silicon interaction, we used the Stillinger-Weber (SW)-type interatomic potential with the repulsive part of the two-body term being splined to the Ziegler-Biersack-Littmart (ZBL) universal repulsive potential.@footnote 2@ For boron-oxygen, We used the Born-Mayer-Huggins potential.@footnote 3@ Effects of dangling bonds and oxygen clusters at SiO@sub 2@/Si interface and silicon vacancy and oxygen vacancy in the oxide film were calculated. We have investigated the SiO@sub 2@ evolution on the silicon surface with rich boron and various defects. The evolution of the structure at the Si/SiO@sub 2@ interface according to the presence of boron atom provided an overview of the behavior of boron dynamics at the Si/SiO@sub 2@. @FootnoteText@ @footnote 1@ T. Watanabe et al., Jpn. J. Appl. Phys. Vol.38 Part 2.No. 4A (1999) pp. L366-L369. @footnote 2@ J. W. Kang, E. S. Kang, H. J. Hwang, will be published in May, J. Kor. Phys. Soc. Vol. 34 (1999). @footnote 3@ J. M. Delaye, V. L-Achille, D. Ghaleb, J. Non-Cry. Solids, 210(1997) 234-242.

SS-WeP20 Cesium-induced Structural Transformation from the Si(113)3x2 to the 3x1 Surface*, C.C. Hwang,* Sung Kyun Kwan University, Korea*; K.S. An,* High Energy Accelerator Organization, Japan*; S.H. Kim, C.Y. Park,* Sung Kyun Kwan University, Korea*; A. Kakizaki,* High Energy Accelerator Organization, Japan

Adsorbates such as H, Na, Cs, etc. on the Si(113)3x2 surface are known to induce a structural transformation to the 3x1 surface. The origin, however, seems to be still unclear due to the lack of informations about the adsorption behavior of several adsorbates as well as the structure of the 3x2 surface. To investigate the adsorption behavior of cesium on the Si(113)3x2 surface at room temperature, we measured the change of workfunction, core level (Si 2p, Cs 4d), and valence band spectra with increasing cesium deposition time by using low energy electron diffraction (LEED) and synchrotron radiation photoemission spectroscopy. As previously reported, the adsorption of cesium induced the structural transformation from the Si(113)3x2 to the 3x1 surface. When cesiums adsorbed on the Si(113)3x2 surface, the workfunction decreased to about 3.2 eV and surface states from dangling bonds disappeared gradually with increasing cesium deposition time. These results indicate that cesiums adsorb preferentially on dangling bond sites at the initial stage of adsorption. We also observed that two shoulders at higher and lower binding energy than the bulk peak in Si 2p core level spectrum from the 3x2 surface disappeared by the adsorption of cesium. Rehybridized surface atoms towards sp@super 2@- and s@super 2@p@super 3@-like configurations thus seem to be changed to sp@super 3@-like ones with the structural transformation. Based on these results, we will discuss the possible origin of the cesium-induced structural transformation at room temperature.

SS-WeP21 Investigations of the Effects of P and Ge on the Desorption of D@sub 2@ from Si(100) and Si(111)*, J.L. Stepnowski, C. Dougherty, G.J. Batinica, M.L. Jacobson, M. Chiu, B.M.H. Ning, J.E. Crowell,* University of California, San Diego

The desorption of D@sub 2@ from Si(100) covered with various concentrations of both P and Ge has been investigated using temperature programmed desorption (TPD). Chemical vapor deposition was used to prepare the surfaces. Phosphorus at different concentrations was deposited at 873K using phosphine as the molecular source gas, and separately, various Ge coverages were prepared by exposing the surface to digermane at approximately 160K. After each exposure, the crystal was flashed to 873K to desorb hydrogen. The resulting P and Ge surface coverage was determined by Auger Electron Spectroscopy. The P,Ge modified Si surface was then exposed to D atoms produced by cracking D@sub 2@ gas with a hot tungsten filament and then a TPD spectrum was taken. Previous studies in our laboratory found that addition of phosphorus alone shifts the @beta@1 desorption state to higher temperatures relative to clean Si(100) while the presence of only submonolayer germanium on the Si surface decreases the @beta@1 peak temperature. This investigation will detail the combined effect of P and Ge on the Si(100) surface. Furthermore, the combined system of P and Ge on Si(111) has been previously examined in our laboratory and a comparison of the effect of these additives on the desorption behavior of Si(100) versus Si(111) will also be presented.

SS-WeP22 Direct Absorption of Thermal H Atoms by Crystalline Silicon: A Narrow Substrate Temperature Window*, J.H. Kang,* Kyung Won University, S. Korea*; S.K. Jo,* Kyung Won University, S. Korea, South Korea*; J. Lee,* Seoul National University, S. Korea*; B. Gong, J.M. White, J.G. Ekerdt,* University of Texas at Austin

Si(100) surfaces exposed to gas-phase thermal-energy hydrogen atoms, H(g), were studied by temperature-programmed desorption (TPD) together with H/D isotope exchange experiments. We find that direct absorption of H(g) into crystalline bulk of Si(100) substrates occurs within a narrow substrate temperature window of 400 - 600 K. The bulk-absorbed hydrogen evolved out molecularly from Si(100) at a temperature 70 - 120 K higher than that of surface-adsorbed monohydride phase (@beta@@sub 1@) in TPD. This bul k-phase hydrogen (@alpha@) uptake increased with increasing H(g) exposure without saturation within our experimental limits. While pre-adsorbed hydrogen atoms on the surface, H(a), were readily abstracted and replaced by D(g), the amount of pre-absorbed H in the bulk remained unchanged by subsequent D(g) exposures. Our result of extensive H/D isotope mixing suggests that absorbed H atoms remain trapped atomically, rather than molecularly, at interstitial sites. We propose a model, in which the (2x1) surface dimer structure of Si(100) serves as a two-way barrier for both direct H(g) absorption and thermal evolution of molecular hydrogen.

SS-WeP23 Low Energy Electron Damage to Condensed Phase Cyclic Ethers Studied by Electron Stimulated Desorption*, L. Parenteau, D. Antic, L. Sanche,* University of Sherbrooke, Canada

Low-energy electron (E@sub i@ < 20 eV) damage to condensed molecules prepared under ultra-high vacuum conditions has been the focus of intense study in recent years.@footnote1@ This research has particular relevance to the field of radiation science as it is well known that a large amount of low-energy secondary electrons are produced along the radiation tract following the interaction of ionizing radiation, the majority of which are created with initial kinetic energies well below 20 eV. At these low energies, fragmentation may occur following dissociative electron attachment (DEA) via the formation of negative ion resonances or by dipolar dissociation (DD). These processes are generally monitored in condensed-phase systems by electron stimulated desorption (ESD) which measures the negative ion yield desorbing from the surface. Below the DD threshold negative ion formation arises exclusively via DEA, whereas above this threshold the ESD yield is dominated by anions produced largely via DD. In recent years, there has been a shift in emphasis towards molecular systems of biological relevance, such as DNA bases,@footnote2@ radiosensitizing 5-halo-uracils and homo-oligonucleotides.@footnote3@ We are now studying the chemical consequences of the interaction of low energy electrons with the deoxyribose backbone of DNA and its constituents. Preliminary results on DEA damage to DNA sugar-like backbone analogues, tetrahydrofuran, 3-hydroxy-tetrahydrofuran and tetrahydrofurfuryl alcohol will be presented. In addition to a core excited resonance observed in the H@super -@ ESD yield near 10 eV incident electron energy, we find significant H@super -@ production via DEA to occur above the DD threshold for incident electron energies near 23 eV. @FootnoteText@ @footnote1@L. Sanche, Scanning Microscopy 9, 619 (1995). @footnote2@D.V. Klyachko, M.A. Huels, and L. Sanche, Radiat. Res. 151, 177 (1999). @footnote3@P.C. Dugal, M.A. Huels, and L. Sanche, Radiat. Res. 151, 325 (1999).

SS-WeP24 Electron- and Photon-stimulated Desorption of Alkali Atoms from Silicon Dioxide Surfaces*, B.V. Yakshinskiy, T.E. Madey,* Rutgers University

As part of a program to probe the mechanisms by which Na and K atoms originate in the atmospheres of the planet Mercury and the Moon, we are studying the electron- and photon-stimulated desorption of Na deposited on model mineral surfaces: amorphous SiO@sub2@ thin films, grown on a Re(0001) substrate. The measurement scheme for electron- stimulated desorption (ESD) of Na atoms includes an efficient pulsed low energy electron source, a highly sensitive detector of Na based on surface ionization, and a time-of-flight technique. For photon-stimulated desorption (PSD), a 500 W Hg arc lamp photon source, a mechanical chopper, and appropriate filters are used. We find that bombardment of Na / SiO@sub2@ surface by ultraviolet photons or by low energy electrons (E > 4 eV) causes desorption of 'hot' Na atoms with the velocity distribution peak at 1000 m/s. The desorption cross section is ~ 10@super-20@ cm@super2@ at 5 eV excitation energy for both ESD and PSD. The ESD yield demonstrates a resonance-like feature at ~11 eV. We interpret the ESD / PSD of Na as occuring via a substrate mediated charge transfer process, in which ionic Na@super+@ is converted to neutral Na, which desorbs. These data provide evidence that DIET mechanisms (e. g., PSD) may contribute as source processes for Na in tenuous planetary atmospheres. Although there are insufficient electrons in the solar wind to produce the observed lunar sodium atmosphere, there appear to be sufficient UV solar photons to maintain the atmosphere by desorbing Na from the surface.

SS-WeP25 Metastable Surface Structure of KTaO@sub 3@(001) by Helium Atom Scattering@footnote 1@*, J.A. Li,* ***T.W. Trelenberg****, E.A. Akhadov, J.G. Skofronick, S.A. Safron,* Florida State University*; L.A. Boatner,* Oak Ridge National Laboratory

Helium atom scattering is used for measurements of the surface structure of KTaO@sub 3@ immediately after cleaving in situ in a UHV scattering chamber. Angular distributions (ADs) of this simple perovskite insulator are measured under destructive interference conditions for steps of one-half the unit cell of KTaO@sub 3@(2Å). Initially the specular peak is very small and is flanked on each side by a satellite peak at ±0.043Å@super -1@. Over a period of one to three hours, depending upon the surface temperature, the specular peak grows in intensity while the satellite peaks decrease in intensity until they essentially disappear. The result is what appears to be a typical AD. A model consisting of uniform-width step-up and step-down terraces is presented which agrees with the initial observations. With increasing time, the terrace widths become more nonuniform and the step heights increase to the lattice spacing of the full unit cell(4Å) due to the mass transport. The first of these developments leads to a reduction of the satellite peak intensities and the second leads to an enhanced specular signal because of the constructive interference. @FootnoteText@ @footnote 1@Supported by U. S. Department of Energy grant number DE-FG02-97ER45635.

SS-WeP26 A Calibrated Adsorption and Thermal Desorption System using Glass Capillary Arrays and a Capillary Valve Flow Source*,* ***R.H. Jackson,*** *B.G. Frederick, D.J. Dwyer,* University of Maine

We demonstrate a calibrated thermal desorption system utilizing a glass capillary array doser as a calibrated beam source. Absolute calibration of the mass spectrometer signal in molecules per second is achieved using both calculated and measured flux distributions from the doser to calibrate the doser flux to the inlet appeture of a differentially pumped thermal desorption mass spectrometer. By a re-parameterization of the formalism of Winkler and Yates,@footnote 1@ we have reduced the order of the necessary integrations from 3 to 2, which simplifies treatment of arbitrarily shaped planar targets. Fourier convolution methods are used to calculate of the flux to a target at any position in a plane parallel to the doser face. These calculations are compared to direct measurements of the doser flux in 3 dimensions. The pressure versus time, measured by a spinning rotor gauge in a gas cell of known volume, determines the flow rate to the doser. The flow closely obeys the simple effusion model after accounting for finite base pressure. A transient molecular flow model is applied to the establishment of the flow from the capillary valve, providing good estimates of the time to steady state for the flow. This Calibrated Thermal Desorption Spectrometer is applied to a study of oxygen on Pd(110) and the coverage results are compared to values from nuclear reaction analysis. @FootnoteText@ @footnote 1@A. Winkler and J. T. Yates Jr. "Capillary array dosing and angular desorption distribution measurements: A general formalism", J. Vac. Sci. Technol. A 6(5), Sep/Oct 1988.

SS-WeP27 Corrosion Inhibition of Aluminum by Self-Assembling Monolayers*,* ***S.M. Wetterer****, P. Dharia, S. Xie, J.J. Donofrio,* Oakite Products, Inc.

Self-assembling monolayers have been evaluated as an alternative to traditional chromium-based treatments for corrosion protection of aluminum surfaces. With good water solubility and long-term solution stability, alkyl phosphonic acids were found to be suitable candidates for the formation of a well-ordered, passivating layer on a series of aluminum alloys. Application process parameters such as immersion time, bath temperature, and anneal time significantly affected the development of the monolayer with implications for the resultant protective benefit of the layer as assessed by humidity and salt-spray corrosion testing. Additional characterization of monolayer-treated panels by SEM and EDAX has provided information regarding monolayer performance over surface defects and edge sites. Modeling of the mechanisms of corrosion protection and eventual breakdown of phosphonate monolayers will be presented.

SS-WeP28 Structure of the (0001) Surface of Hafnium and Hafnium Diboride and of Epitaxial Thin Films of Hafnium Diboride Grown on Hafnium*,* ***R. Singh****, C.L. Perkins, M. Belyansky, M. Trenary,* University of Illinois, Chicago

Scanning tunneling microscopy (STM), x-ray photoelectron spectroscopy (XPS), and low energy electron diffraction (LEED) have been used to investigate the surface structure of single crystals of Hf, HfB@sub 2@, and epitaxial thin films of HfB@sub 2@ grown on a Hf substrate through the thermal decomposition of diborane. A comparison of the properties of HfB@sub 2@(0001) and Hf(0001) is of interest because the topmost atomic layer of both surfaces consists of a close-packed two-dimensional array of Hf atoms with lattice constants that differ by only 1.7%. In the bulk structure of HfB@sub 2@, the (0001) Hf atom planes are hexagonal close-packed and are separated by 0.348 nm. A graphite-like honeycomb lattice of boron atoms lies between the Hf planes. A clean well-annealed HfB@sub 2@(0001) surface is found to consist of Hf-terminated terraces separated by 0.35 nm with no boron layers exposed. When the HfB@sub 2@ sample is not well-annealed or when contamination is present, reconstructed surfaces are observed with both LEED and STM, including a (3x3) structure induced by carbon. The Hf(0001) surface consists of flat (0001) terraces separated by monoatomic steps 0.25 nm in height. The high reactivity of the group IV metals is reflected in the difficulty in obtaining contamination free images of the Hf surface. From the determination of the basic structural features of the HfB@sub 2@ and Hf surfaces by STM, patches of Hf and HfB@sub 2@ can be clearly distinguished in STM images acquired during different stages in the growth of epitaxial thin films of HfB@sub 2@ on a Hf substrate. The thin film growth mechanism can thereby be inferred from such images.

SS-WeP29 Molecular-scale Origins of the Surface Memory Effect at a Liquid Crystal - Solid Interface*,* ***D.M. Scott****, A.J. Brackley, J.D. Mougous, K.M. Foland, D.L. Patrick,* Western Washington University

The surface memory effect (SME) describes the phenomenon in which an initially isotropic surface is rendered anisotropic through contact with anisotropic medium, such as a liquid crystal (LC) fluid. At a LC - solid interface, the SME leads to imprinting of the director orientation onto the surface, which can in turn induce uniform alignment in the bulk LC fluid. The SME is important in LC - based opto-electric devices such as liquid crystal displays. We studied the SME in LC droplets on a polycrystalline graphite substrate using polarized optical and scanning tunneling microscopy (STM). A single crystalline monolayer with macroscopically uniform orientation was prepared by depositing material from the LC droplet in an external magnetic field. The system was found to retain memory of the original bulk orientation, even when the field was removed and the LC was heated beyond its isotropic transition temperature. Loss of the SME coincided with monolayer melting. Comparison of STM images with optical micrographs establish a direct link between molecular alignment in the monolayer adsorbed to the graphite substrate and bulk LC director orientation.

SS-WeP30 Investigation of the Dehalogenation of 1,1-Dichloroethene on Pd(111) Studied by Laser-Induced Thermal Desorption Fourier Transform Spectroscopy (LITD-FTMS)*,* ***D.E. Hunka****, D.P. Land, D.C. Herman,* University of California, Davis

The chemistry of chlorinated ethenes on transition metal surfaces is of great interest due to their prevalence as contaminants in groundwater. The decomposition of geminal dichloroethene (g-DCE) on a clean Pd(111) surface is investigated using thermal desorption spectroscopy (TDS) and laser-induced thermal desorption with FT mass spectrometry (LITD-FTMS). Preliminary results of g-DCE decomposition show that HCl is the major reaction product. The TDS studies have been performed as a function of coverage. At very low coverages, only one peak of HCl is seen to desorb in the range of ~600 K - 1000 K. As coverage increases, a significant portion of g-DCE desorbs intact, the HCl peak shifts to lower temperatures and a second HCl peak grows in with a Tp= 450 K, indicating a step-wise decomposition. At these higher coverages of g-DCE, separate TDS experiments monitoring hydrogen evolution from the surface show a sharp peak at 474 K (in between the two HCl traces). Interestingly, the LITD survey experiments reveal decomposition of g-DCE occurs by 150 K with the concomitant appearance of HCl. These results indicate that both C-H and C-Cl bond cleavage happens at low temperatures, although no chloroacetylene is produced as a second product, which would be indicative of an @alpha@-@beta@ elimination. Further decomposition of the surface intermediates occurs to yield a second formation of HCl which is subsequently liberated from the surface.

SS-WeP31 CV, XPS, SIMS and ISS Examination of Zirconium Passive Film Breakdown in the Presence of Sulfate, ***R Schennach,*** Lamar University &Texas A&M University; *A. Mamun, N. Kunamneni, D.L. Cocke,* Lamar University

Passive films on zirconia have been prepared by potentiodynamic polarization in the presence of a range of anions and at various pH values. Sulfate has been found to produce unique transpassive peaks that appear to be associated with an amorphous to cyrat alline transitionand subsequent enhanced species transport along the resulting grain boundaries. The passive film breakdown can be qualitatively described by E@sub np@ = E@sub c@ + @eta@ + @PHI@ +E@sub inh@. Where E@sub np@ is the pitting potential, E@sub c@ the corrosion potential in acidified solution, @eta@ the polarization necessary to obtain a current density high enough to maintain acidity inside the pit, @PHI@ the potential drop inside of the pit and E@sub inh@ the contribution to pitting potent ial resulting from inhibitors present. XPS, SIMS and ISS have been used to characterize the films before and after the passive film breakdown. The results of these surface studies along with the variation in CV scans have been used to describe the process and to present a model that involves either IR drop and/or local acidification. The involvement of chemically bound water oxidation and local oxygen evolution are presented as well.

SS-WeP33 Composition and Orientation at the Surface of a Room-Temperature Ionic Liquid Observed by Direct Recoiling Spectrometry, ***P.R. Watson,*** Oregon State University, U.S.; *T.J. Gannon, G. Law,* Oregon State University; *A.J. Carmichael, K.R. Seddon,* Queen's University, Ireland

Direct recoil spectrometry (DRS) has recently been applied to investigate the structure and orientation at the surface of low vapor-pressure liquids. Room temperature ionic liquids are generating considerable interest as low vapor-pressure clean technology solvents. We report the first measurements of the composition and molecular orientation at the surface of the room temperature ionic liquid - 1-butyl-3-methylimidazolium hexafluorophosphate, [bmim][PF@sub6@]. Recoil spectrometry using rare gas ions on continuously refreshed liquid surfaces in vacuo shows that neither ion is significantly enriched in the surface. The average orientation of the cation is with the plane of the ring vertical. The cation ring is rotated about an axis through its center such that the nitrogen atoms and side chains are deeper in the surface with the surface normal passing between the two nitrogen atoms (with an estimated error of ±30°).

SS-WeP34 Surface Structures of @beta@-(BEDT-TTF)@sub 2@PF@sub 6@ Induced by Its Polar Surface Characteristics, ***M. Ishida,*** University of Tsukuba, Japan; *T. Mori,* Tokyo Institute of Technology, Japan; *H. Shigekawa,* University of Tsukuba, Japan

Bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF or ET) based organic compounds, one of the low-dimensional conductors, are distinct from the others due to their polar surface characteristics. For @beta@-(BEDT-TTF)@sub 2@PF@sub 6@, an ordered-defect structure was observed on the anion (PF@sub 6@) surface similarly as the typical reconstructions of the inorganic polar surfaces. And characteristic properties such as superstructures and fluctuation of surface structures were observed on the cation (ET) surface. On the other hand, it is well known that @beta@-(BEDT-TTF)@sub 2@PF@sub 6@ undergoes a metal-insulator transition at 297 K, and formation of the 2x|c| superstructure due to 2k@sub F@ CDW is confirmed by X-ray diffraction. However, several superstructures with considerably longer modulations were observed by STM at 285 K instead of the 2x|c| superstructure. From the results of the STM, AFM, XPS studies, and molecular orbital calculations, the observed cation surface structures were concluded to be influenced by charge localization, relaxation of individual molecules, and symmetry breaking in the molecular relaxation. Concerning the modulated CDW phases, susceptibility @chi@(Q) for the surface layers was calculated in order to investigate the origin of the larger modulations, by taking into account the change in the molecular charge on the polar surface. As a result, the observed STM result were in good agreement with the CDW structure derived from the susceptibility calculation.

SS-WeP35 Free Radical Based Amination of Polymeric Interfaces, *H. Fairbrother,* ***A. Wagner****, K. Han, A. Vaught,* Johns Hopkins University

The introduction of nitrogen containing functionality into organic surfaces is often used to modify interfacial characteristics, including permeability, wettability, adhesion, friction, wear and biocompatibilty. Compared to wet-chemical treatments for surface modification vacuum-based technologies are dry, fast and environmentally benign. Compared to the more traditional ion and plasma based modification treatments, the use of gas phase radicals is a relatively underdeveloped component with considerable promise. For example, nascent radical kinetic energies are typically in the range of 0-5eVs in contrast to the several hundred eVs of energy typically associated with ions. To address this issue a new NH radical source, based upon the thermal pyrolysis of hydrazoic acid (HN3) has been developed and characterized using mass spectrometry. Results from the interaction of NH radicals with thiol-based self-assembled monolayers using mass spectrometry, infrared spectroscopy and X-ray Photoelectron Spectroscopy will also be presented.

SS-WeP36 An Ultra High Vacuum Compatible Matrix Assisted Laser Desorption/Ionization Time-of-Flight Mass Spectrometer, ***T.L. Porter,*** *S. Hermann,* Northern Arizona University

The emerging technique of matrix assisted laser desorption/ionization (MALDI) time-of-flight mass spectrometry allows for the mass determination of surface bound polymeric materials that suffer from fragmentation effects using conventional MS techniques. Using MALDI, the sample to be analyzed is combined with a strong UV absorbing "matrix", such as 3-hydroxypicolinic acid or 2,5-dihydroxybenzoic acid. Short UV laser pulses desorb the matrix plus sample material from the topmost sample surface, while simultaneously gently ionizing the sample material. The ionized species are then injected into a time-of-flight analyzer for mass determination. The gentle ionization process allows polymers and bio-materials on surfaces that would normally suffer from fragmentation effects to be detected intact. In this paper, we describe an ultra-high-vacuum MALDI instrument that has been constructed from primarily off-the-shelf components at minimal cost. This instrument may be used to detect the presence of pico-mole amounts of material with atomic weights from a few hundred to over one hundred thousand.

SS-WeP37 Iodobenzene Reactions and cis-1,2-Dichloroethene Chemistry on Pd(111) Studied by Laser-Induced Thermal Desorption Coupled with Fourier Transform Mass Spectroscopy (LITD-FTMS), ***D.M. Jaramillo****, D.P. Land, D.E. Hunka,* University of California, Davis

Halocarbons are important compounds for obtaining alkyl groups on metal surfaces. The thermal and photo dissociation of the carbon-halogen bond allows us to probe the chemistry of hydrocarbon fragments which have shown to be transient intermediates in catalytic processes. In addition, the reactions of halocarbons on metal surfaces relates to the remediation of chlorinated solvents from waste water. Elucidation of the mechanism of halocarbon decomposition will aid in determining better catalysts for remediation. The chemistry of iodobenzene and cis-1,2-dichloroethene have been investigated on Pd(111). Submonolayer iodobenzene adsorption at 90 K results in the formation of phenyl groups and iodine on the surface. The phenyl groups are hydrogenated by subsurface hydrogen to form benzene which desorbs around 500 K. Higher exposures of iodobenzene show iodobenzene desorbing at 200 K and benzene observed only at 140 K. The adsorbed iodine changes the reactivity of iodobenzene. Molecular desorption of cis-1,2-dichloroethene occurs at 160 K for low exposures and at around 200 K for higher exposures. Hydrogen is seen to desorb around 300 K for even the lowest exposure studied. No HCl was observed in TDS or LITD.

SS-WeP38 Energy Transfer in Collisions of Nitric Oxide with Ordered Molecular Adlayers, *M.K. Ainsworth, V. Fiorin,* ***M.R.S. McCoustra****, M.A. Chesters,* University of Nottingham, UK

Detailed dynamical measurements have been made of the scattering of nitric oxide from well-characterised and well-ordered monolayers of carbon monoxide (CO) and ethylidyne (CCH@sub 3@) adsorbed on a Pt(111). The scattering dynamics have been probed using a combination of molecular beam and laser spectroscopic techniques for incident NO translational energies in the range 5 to 50 kJ mol@super -1@ at substrate surface temperatures from 100 to 300 K. Time-of-flight measurements were used to determine the translational energy of the scattered NO, while resonance-enhanced multiphoton ionisation was used to recover its rotational quantum state distributions. The results of both types of experiment will be reported. Significant loss of incident NO translational energy is observed and evidence from these measurements suggests that scattering occurs into both a direct inelastic scattering channel and a trapping-desorption channel. The scattering dynamics from both adlayers are found to be similar, with only slight differences that may be interpreted in terms of different interaction potential strengths.

SS-WeP39 Surface Diffusion of Photogenerated Hydroxyl Radicals as Probed by FTIR, ***Y. Paz****, H. Haick,* Technion-IIT, Israel

Titanium Dioxide is a well-known photocatalyst for water and air treatment as well as for catalytic production of gases. For many organic materials, destruction of contaminants occurs through an oxidation mechanism, where hydroxyl radicals formed on the surface of the catalyst attack adsorbed compounds. Structures comprised of photoactive titanium dioxide and inert adsorbents may promote the overall performance of the photocatalyst by concentrating molecules, that usually do not adsorb on TiO@sub 2@, at the vicinity of the photocatalyst. Furthermore, one may consider the modification of the inert domains to achieve selective physisorption of contaminants of interest. This selectivity can be achieved by coating the inert areas with chemisorbed organic molecules, tailored for specific physisorption of the contaminants. The growing interest in such combined structures is strongly coupled with the debate over possible surface diffusion of the oxidizing species (namely OH radicals), which might migrate to the inert domains where they might mineralize the organic templates. The destruction of templates of alkyl-trichlorosilane organized organic monolayers, chemisorbed in the vicinity of TiO@sub 2@ domains, is studied. Based on in-situ FTIR measurements, it is shown that OH radicals, formed on the titanium dioxide micro-domains, are capable of inducing the mineralization of the fixed chemisorbed aliphatic chains, within minutes, even when these chains are located as much as 20 microns away from the titanium dioxide domains. These results, measured as a function of domain size and surface temperature, are now being evaluated in order to deduce surface diffusion parameters.

SS-WeP40 The Interactions of Azomethane and Methyl Radical with Cu(111)*, **P. Chuang,*** National Taiwan University, Taiwan*; Y.L. Chan,* Academia Sinica, Taiwan*; C.H. Chuang,* National Central University, Taiwan*; S.-H. Chien, T.J. Chuang,* National Taiwan University, Taiwan

We have employed TPD, XPS, LEED and HREELS to investigate the interactions of CH@sub 3@ radicals and CH@sub 3@N@sub 2@CH@sub 3@ molecules with Cu(111). The subject is of interest@footnote@ due to the importance of the radical in many heterogeneous reactions involving hydrocarbons. It is found that distinctive adsorption states exist for azomethane on Cu at 90K depending on surface coverage. Molecular desorption is detected at 205K, 145K and 120K corresponding to the first chemisorbed layer, the second layer and the bulk-like multilayer, respectively. Both first-order and zero-order desorption kinetics are observed. Methyl radicals can be chemisorbed on Cu(111) at 300K showing partial decomposition to CH@sub 2@(ads) and H(ads), mediated possibly by defect sites. CH@sub 3@ thermal desorption signals exhibit two channels at about 360K and 440K, corresponding to the second-order and the first-order desorption kinetics. The behavior is closely related to H and CH@sub 3@ coadsorption and reaction during the desorption process. The results of TPD, XPS and HREELS are correlated with each other and compared with previous work. @FootnoteText@ @footnote 1@T.J. Chuang, Y.L. Chan, P. Chuang and R. Klauser, J. Electr. Spectr. Relat. Phenom. 98-99, 149 (1999).

Applied Surface Science Division
Room 6A - Session AS-ThM

Real World Surface Analysis

Moderator: T. Barr, University of Wisconsin, Millwaukie

9:00am **AS-ThM3 The Real World: Surface Analysis Applications and Innovations in Industry*, S.J. Pachuta,*** 3M **INVITED**

The term "real world" surface analysis is often used in opposition to "academic" surface analysis. The distinction is conventionally viewed as being a matter of single crystal studies under ultra high vacuum in the academic case, vs. everything else in the real world case. In reality there is, of course, some overlap between the two, but it is true that industrial analysts must often deal with unknown materials under less than ideal conditions. The following is a far from exhaustive list of the challenges: samples with fingerprints and surface environmental contamination; volatile materials; buried layers, both elemental and organic; complex mixtures such as copolymers and blends with multiple additives; submicron features and defects, possibly on the surface but often buried; insulators; samples too large for most vacuum systems, but which must be preserved and cannot be cut; inhomogeneous materials. More often than not, a multi-instrument approach is needed to address industrial surface analysis problems. The three techniques of x-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), and secondary ion mass spectrometry (SIMS) comprise the backbone of most industrial surface analysis laboratories. Other techniques like infrared spectroscopy and atomic force microscopy are also being increasingly utilized. An important--and sometimes overlooked--aspect of surface analysis is sample preparation, which often turns out to be the key to solving a problem. This talk will use examples from a diverse industrial laboratory to illustrate the synergism between the various surface analysis methods. Emphasis will be placed on organic materials, since a large part of industrial analysis is concerned with polymers and other organics. New sample preparation methods for XPS and time-of-flight SIMS will be described which extend the capabilities of these techniques.

9:40am **AS-ThM5 Effect of Sputtering Gas on Cleaning Al-Based Intermetallics and the Determination of Surface Compositions based on Auger Analysis*, C.J. Jenks,*** *T.E. Bloomer, M.J. Kramer,* Ames Laboratory*; J.W. Burnett,* Iowa State University*; D.W. Delaney, T.A. Lograsso, M.F. Besser, D.J. Sordelet, P.A. Thiel,* Ames Laboratory

Argon is the typical gas of choice for sputtering single crystals in preparation for ultrahigh vacuum studies. However, the use of argon when cleaning Al-based intermetallics leads to preferential etching of Al. This can be a problem because of potential phase changes and the need for a consistent surface composition after annealing. We have examined the extent of this preferential etching as a function of ions/cm@super 2@ for helium, neon, argon, and krypton. The intermetallic substrate has a bulk composition of Al@sub 72.8@Pd@sub 18.6@Mn@sub 8.6@. We find for this material that the steady state Al concentration at the surface is about the same for all the sputtering gases examined. However, the number of ions/cm@super 2@ (which is related to time) depends on the sputtering gas used. Also discussed will be the determination of surface composition of Al-based intermetallics by Auger Electron Spectroscopy. For these materials, in particular, the sensitivity factors will differ greatly between the pure elements and the compound matrix because of changes in electron escape depth, electron backscattering, and atomic density. We find that the use of certain standards can lead to erroneous results.

10:00am **AS-ThM6 Failure Mechanisms of Adhesively Bonded Hot Dipped Galvanised Steel Studied by Small Area XPS*, R.G. White,*** VG Scientific, UK*; M.F. Fitzpatrick, J.F. Watts,* University of Surrey, UK

One of the most important requirements of an adhesive joint is the retention of strength for an acceptable time on exposure to a hostile environment. Durability is recognized as one of the most significant problems in the adhesive bonding in industry. In a previous paper, small area XPS established that electrochemistry was responsible for initial bond degradation in a phosphated hot dipped galvanised steel (HDGS) lap joint.@footnote 1@ This paper reports a surface analysis investigation of the failure mechanism of adhesively bonded hot dipped galvanized steel that has been exposed to a hostile environment. The failed lap shear joints show areas of apparent interfacial failure, however, these regions are limited to thin strips at the end of the overlap. These "initiation zones" seem to be a result of environmental exposure and appear to act as initiation sites for crack propagation on mechanical testing, acting as "notch like" features. The study of these areas of the failed surface using small area XPS (15 micron resolution) is reported in this paper, with a view to establishing the role of electrochemical activity at the crevice tip and its role in the subsequent joint failure. Acknowledgement : The authors wish to thank British Steel Strip Products and Welsh Technology Centre for the provision of a Research studentship (MFF) and for permission to publish this paper. @FootnoteText@ @footnote 1@J.F.Watts and M.F.Fitzpatrick Surf. Interf. Anal. in press.

10:20am **AS-ThM7 Novel X-ray Sensor Suite for In Situ Optimization of Thin Film Architectures*, L.L. Fehrenbacher*,** *D. Palaith, C. Deaton, J. Ullrich,* Technology Assessment & Transfer, Inc.

Advances in compact, high energy x-ray sources and sensitive detectors are creating new opportunities for the use of x-rays for real time and near real time interrogation of thin film properties. A design approach that combines x-ray diffraction, florescence and reflectivity measurements with a thin film deposition system is described. Phase, composition, surface and interfacial roughness, thickness and density of thin films can now be monitored during a thin film deposition process enabling improved control over process deposition parameters. Details of the equipment and examples of the systems used for rapid development of new multilayer thin film architectures as well as production control are provided.

10:40am **AS-ThM8 A 300mm SAM, with EDX and FIB for Full Wafer Defect and Thin Film Characterization*, Y. Uritsky,*** Applied Materials, Inc.*; C.R. Brundle,* Applied materials, Inc.

As design rules shrink and thin film stacks get thinner, the semiconductor equipment manufacturing industry is forced to move to more sophisticated approaches for its particle defect and thin film characterization needs, including surface and thin film analysis. In the past we have occasionally supplemented our full wafer (200 mm) SEM/EDX small particle analysis work by SAM, using small cut up pieces of the wafer. We have now installed the first full 300 mm wafer SAM (Smart 300 from PHI), on which we also have traditional EDX and also FIB. The capabilities of this instrument are briefly described here and examples are given of its use to a) find small defects based on navigation from light scattering files, b) comparatively analyze small particles using Auger, EDX, and FIB sectioning, and c) profile films to examine interfaces. With respect to a) above, since light scattering files are usually quite inaccurate (the predicted coordinates can easily be in error by 100's of µm's), it can be very time-consuming, if not impossible, to re-find very small particles (0.1 µm) with low SEM or Auger contrast. Use of a 300 mm capable dark field optical bench/wafer marker (MicroMark 5000) system to update the particle coordinates with +/- 5 µm) accuracy and/or to create laser-made fiducial marks, can accelerate the subsequent particle re-detection/analysis SAM procedure by a factor of 10. Another particular concern to us, since it is a widely used element in semiconductor processing and is very aggressive, is the relative ability of Auger, EDX, and FIB sectioning Auger and EDX, to reliably detect F as opposed to removing it under the probe beam. This is discussed.

11:00am **AS-ThM9 A Study of the Surface Chemistry and Physical Properties Related to Adhesion of the Polyimide Passivation Layer by XPS, FTIR, and Contact Angle Measurements*, T. Jiang*,** Micron Technology Inc.*; C.A, Bradbury,* Micron Technology Inc., US*; M. Canavan,* Micron Technology Inc

Adequate die-to-leadframe adhesion is necessary for lead on chip (LOC) package integrity during and after the manufacturing process. Poor adhesion may result in a variety of defects such as die adhesion failure, marginal wire bond, broken wire, and bent leads ultimately leading to electrical failure. Adhesion between the LOC tape and the polyimide passivation is affected by the surface properties of both materials. Understanding the relationships between these properties is important for the elimination of adhesion failures at die attach and for the continuous improvement of the manufacturing process. To this end, die which fail at attach are analyzed and compared with die which exhibit good adhesion characteristics. This study focuses on the surface chemistry and physical properties of the passivation layer using X-ray photoelectron spectroscopy (XPS), Fourier transform infrared spectroscopy (FTIR), atomic force microscopy (AFM), and surface energy. Molecular concentrations and orientations are investigated and related to adhesion failures at die attach.

11:20am **AS-ThM10 Diffusion of Large Molecules on Metallic Surfaces using TOFSIMS*, R. Avci*,** *S.E. Maccagnano,* Montana State University*; G.L. Gresham, G.S. Groenewold,* Idaho National Engineering and Environmental Laboratory

The environmental contamination of clean surfaces creates challenging problems in practical surface analysis. In most cases the contamination is caused by a contact between a dirty and a clean surface and the subsequent diffusion of the contaminant over the clean surface. In this presentation a semi-quantitative study of the diffusion process of large molecules such as polydimethylsiloxane and tributyl phosphate on metallic surfaces will be presented. Using imaging time-of-flight secondary ion mass spectroscopy (ToFSIMS) we have monitored the diffusion of these molecules by first absorbing them on the surface of a fiber such as linen and nylon and then placing the fiber in contact with a metallic surface such as a gold-coated silicon wafer. ToFSIMS spectra are taken as (a) a function of distance from the contact point and (b) a function of time from moment of contact to determine the diffusion properties of these molecules on the surface. Our preliminary observations show that these molecules rapidly diffuse away from the contact point on the surface of the metal.

11:40am **AS-ThM11 Identification of Surface Chemical Functional Groups in Reverse Osmosis Membranes: An X-ray Photoelectron Spectroscopy Study***, **S.D. Beverly**, S. Seal, S.K. Hong,* University of Central Florida

Membrane filtration including reverse osmosis (RO) has emerged as a viable drinking water treatment technology that offers a versatile approach to meeting multiple water quality objectives. Due to fouling and membrane failure, however, wide use of membrane processes for municipal water supplies has not become the reality that it could be. This study is an attempt to identify surface functional groups and chemical changes in surfaces of RO membranes during operation, which would give clues to the nature of the membrane failure. Since the depth of the RO membrane skin layer is less than 50 angstroms, X-ray Photoelectron Spectroscopy (XPS) was chosen to be a practicable analytical tool for this research study. Three commercial RO membranes made of organic polymers of polyamide or cellulose acetate were investigated. These membranes were chosen because of specific characteristics such as chlorine degradation, biological degradation, or fouling resistant coatings. For each membrane, a baseline spectrum was taken and then a sample of the membrane used to treat river water in Tampa, Florida was tested. Each sample was thoroughly rinsed in DI water and allowed to dry before XPS analysis. XPS analysis clearly showed a distinct uptake of chlorine in the polyamide membrane, a probable reason for failure in the drinking water industry. The cellulose acetate membrane showed evidence of amino acids, an indicator of digestion by an unidentified microbe. Based on the findings of this report, future studies are being considered to further investigate chlorine uptake by RO membranes. The studies will include charting chlorine uptake over time and finding limiting factors to chlorine uptake.

Biomaterial Interfaces Group
Room 613/614 - Session BI-ThM

Biomineralization

Moderator: J.J. Hickman, The George Washington University

8:20am **BI-ThM1 Nucleation and Growth of Calcium Phosphate on Self-Assembled Monolayers***, **C.C. Chusuei**,* Texas A&M University*; B.J. Tarasevich,* Pacific Northwest National Laboratory*; D.L. Allara,* Pennsylvania State University*; M.J. Van Stipdonk, E.A. Schweikert, D.W. Goodman,* Texas A&M University

Calcium phosphate (CP) was adsorbed onto 16-carbon chain length self-assembled monolayers (SAMs) with various terminated functional groups from solution simulating ionic conditions found in blood plasma at the bone growth region at various exposure times to observe the onset of nucleation growth. X-ray photoelectron spectroscopy (XPS) was used to quantitate nucleation and growth of CP on the surface and compared with ellipsometric measurements. Secondary ion mass spectrometry (SIMS) was used for speciation, monitoring transformation from amorphous phases to hydroxyapatite and comparing them to standardized CP powders.@footnote 1@ Accelerated nucleation and growth of CP on anionically charged SAMs terminal functional groups, -COOH and -SO@sub 4@H, was readily observed at 310 K (consistent with physiological conditions) relative to room temperature (298 K). No growth was observed on the -CH@sub 3@ terminated SAMs. @FootnoteText@ @footnote 1@ Chusuei, C. C.; Van Stipdonk, M. J.; Justes, D. R.; Schweikert, E. A.; Goodman, D. W. Anal. Chem. 1999, 71, 149-153.

8:40am **BI-ThM2 Surface Modification of a Model Biomaterial by UV-Laser and/or Electron Beam Irradiation@footnote 1@***, **M.L. Dawes**,* Washington State University*; Y. Kawaguchi,* Chugoku National Industrial Research Institute, Japan*; S.C. Langford, J.T. Dickinson,* Washington State University

Single crystal brushite (CaHPO@sub 4@@super .@2H@sub 2@O) is a model hydrated phosphate for studies of surface modification, etching, and biocompatible film growth by laser ablation. In this study we show that significant chemical and morphological changes are produced on such crystal surfaces by irradiation with electron and UV-laser beams. These changes are due to both photoelectronic and thermal effects, principally involving the anion, and are associated with high densities of point defects. We compare the spectroscopic and morphological changes generated by laser and electron beam irradiation as well as by thermal treatment in vacuum. All three treatments dehydrate the surface material; the resulting material forms subsurface, micron-sized platelets which can be exposed by spontaneous fracture of the surface layer. Spectroscopic evidence for reduced forms of phosphorus (primarily pyrophosphate but also elemental phosphorous) are observed on the treated material. Mass spectroscopy of laser-induced emissions from treated material show significant O@sub 2@ and PO@sub x@ emissions, consistent with this reduction. @FootnoteText@ @footnote 1@ This work is supported by the Department of Energy (DE-FG03-98ER14864) and the National Science Foundation (CMS-98-00230).

9:00am **BI-ThM3 Synthesis and Surface Characterization of Peptide-Modified Interpenetrating Polymer Networks that Control Biomineralization***, **K.E. Healy**, T. Barber,* Northwestern University*; D.G. Castner, S.L. Golledge,* University of Washington **INVITED**

A major limitation in the performance of materials used in the medical device and pharmaceutical industries is that they lack the ability to integrate with biological systems through either a molecular or cellular pathway. We have designed and synthesized interfacial interpenetrating polymer networks (IPNs) that resist non-specific protein adsorption, and can be modified to tether bioactive groups such as peptides that mimic cell binding domains found on ECM molecules. An IPN was created by sequential photoinitiated synthesis of a thin layer of poly(acrylamide) [P(AAm)] followed by a secondary photoinitiation step using poly(ethylene glycol) [PEG] based monomers to create the network. Tethering of peptides was achieved by photoinitiated synthesis of PEG-monomethyl ether monomethacrylate, acrylic acid (AAc) and N,N-methylene-bis-acrylamide into the P(AAm) layer. A spacer of bisamino PEG (3400 MW) was then bonded to the AAc through a carbodiimide reaction. As a specific example of coupling bioactive molecules to the surface, peptides from the cell binding domain [CGGNGEPRGDTYRAY] and heparin binding domain [FHRRIKA] of bone sialoprotein were tethered to the remaining free PEG amine moiety via a sulfosuccinimidyl 4-(N-maleimidomethyl)cyclohexane-1-carboxylate cross linker. Surfaces were characterized by contact angle measurements, spectroscopic ellipsometry, and X-ray photoelectron spectroscopy. The surface characterization confirmed the formation of the IPN and subsequent immobilization of the peptide. These surfaces resisted protein deposition and neither supported cell attachment nor growth without immobilization of the RGD-based biomimetic peptide from bone sialoprotein. Molecular modification of the non-adhesive IPN using a RGD-containing peptide led to rapid bone cell attachment independent of the presence of serum proteins, and subsequently to normal cell proliferation and normal phenotypic expression (e.g., synthesis of mineralized matrix).

9:40am **BI-ThM5 Osteoblast Behavior on Surfaces with Varied RGD Peptide Surface Concentrations Prepared Using Gold-Thiol Self-Assembly, G.D. Moodie**, *D.M. Ferris, R.F. Henn, N.J. Wimmer,* Brown University*; R.F. Valentini,* Brown University / Rhode Island Hospital

In this work we evaluate the response of osteoblasts to changing concentrations of the integrin-binding RGD peptide immobilized on gold-coated surfaces. Surfaces were prepared by evaporating 100 Å of titanium onto glass cover slips followed by 800 Å of gold. The peptide Arg-Gly-Asp-Cys (RGDC) and the diluent Cys were bound to the gold through the Cys thiol. 1:0, 1:1, 1:10, 1:100, 1:1000, 1:10000, and 0:1 RGDC:Cys solutions were tested. XPS and SIMS verified peptide immobilization. Osteoblasts isolated from 6-day old rat calvaria were plated at a density of 10,000 cells/cm@super 2@ for one hour and then fixed. Co-localization of actin and vinculin indicates the presence of integrin-based focal adhesions. Vinculin was stained with mouse anti-human vinculin IgG and a rhodamine conjugated secondary antibody. Actin staining was done with FITC / phalloidin. Peptide stability was first assessed by aging uncoated, RGDC coated, and fibronectin coated substrates for 3, 9, 14, and 28 days in serum-free media. Co-localizations were observed on 85-90% of cells on

RGDC substrates that had been aged for 3 to 28 days. In contrast, co-localization on fibronectin coated surfaces showed a steady decline with aged specimens and was at the level of plain gold by day 28 (about 30%).The percent of cells showing co-localizations, the number of co-localizations per cell, and cell area all decreased as peptide concentration decreased and were statistically different from 100% RGDC at and below the 1:100 dilution. This study shows that RGDC binds to gold surfaces and influences osteoblast response in a dose-dependent fashion.

10:00am **BI-ThM6 Molecular Recognition at the Protein-Biomineral Interface***, **J.R. Long**, W.J. Shaw, G.P. Drobny, P.S. Stayton, P. Bower,* University of Washington

Biological organisms exhibit sophisticated crystal engineering capabilities that underlie the remarkable material properties of mineralized tissues such as bone and nacre. While nature's biomineralization processes are a complex blend of finely controlled nucleation and growth events that are not currently well understood, it is known that organisms produce acidic proteins which play a key directoral role in controlling biological crystal growth. We have taken a systematic approach with model proteins and biological proteins and peptides to elucidate how small, acidic proteins interact with biological crystals and control their growth rates. Solid-state NMR results investigating protein conformation and orientation on HAP surfaces will be reported.

10:20am **BI-ThM7 Kinetics and Interfacial Energy Studies of Biomineralization***, **G.H. Nancollas**, W. Wu,* State University of New York, Buffalo **INVITED**

The ability of surfaces to nucleate minerals such as the calcium phosphates is important in a wide range of biological events. The kinetics of crystallization and dissolution of the mineral surfaces has received considerable attention from the point of view of parameters such as solution composition, ionic strength, pH, temperature, and solid surface characteristics. However, a factor which is usually ignored in discussions of such induced crystallization reactions is the surface free energy of the nucleus/substratum interface. The Constant Composition method is especially useful for investigating the mechanisms of these reactions and surface free energies, measured using thin layer wicking methods can be used to corroborate crystal growth and dissolution mechanisms determined from kinetics experiments. Kinetic studies have been made using calcium phosphate phases such as dicalcium phosphate dihydrate (DCPD), octacalcium phosphate (OCP), hydroxyapatite (HAP), and fluorapatite (FAP). The much smaller interfacial tensions of OCP and DCPD in contact with water as compared with those of HAP and FAP support the widely held suggestion that the former phases are precursors in HAP and FAP biomineralization. On substrata consisting of minerals, polymers or typical implant materials such as the titanium oxides, the ability of the surfaces to nucleate calcium phosphate minerals is closely related to the magnitude of the interfacial energies.

11:00am **BI-ThM9 Incorporation of Dye Molecules into Calcium Oxalate Host Crystals***, **L.A. Touryan**, R.W. Gurney,* University of Washington*; M.J. Lochhead,* University of New Hampshire*; B. Kahr, V. Vogel,* University of Washington

Biological systems direct inorganic mineral synthesis and subsequent composite growth via molecular interactions between macromolecules and mineral phases. However, describing the relationship between the organic and inorganic molecules and their interactive functions at the molecular level remains difficult. Exactly how additives orient within host lattices is not known, as biomineral crystals accommodate their presence but they do not give rise to sufficient intensity in x-ray diffraction studies. Nevertheless, it is this integration of large biomolecules into much smaller unit cells that profoundly changes the materials properties of biominerals and make their synthetic recreation desirable for novel material design and the enhanced biocompatibility of biomedical implants. Here we discuss the use of sensitive optical techniques, in conjunction with modeling, to determine the spatial orientation of organic additives within the host lattice of a calcium biomineral. We have found that common aryl-carbonium dye molecules such as eosin and fluorescein incorporate into the lattice structure of calcium oxalate, the primary biomineral of kidney stones. These dyes tend to incorporate along the fastest growing crystal planes, and can be detected through fluorescence microspectroscopy. We have measured the intensity of polarized fluorescence on two well-developed crystal faces, calculated dichroic ratios, and used the data to model the direct orientation of the transition dipole moments of organic dyes that incorporate within the inorganic host lattice.

11:20am **BI-ThM10 Molecular Orientation in Artificial Joint Polymers: Characterizing the Precursors of Wear with Soft X-ray Absorption***, **D.A. Fischer**,* National Institute of Standards and Technology*; S. Sambasivan,* Brookhaven National Laboratory*; M. Shen,* University of Maryland, College Park*; S. Hsu,* National Institute of Standards and Technology

Over half a million patients receive artificial joint replacements annually and practically all the replacements consist of a sliding pair represented by a polymer (ultra-high molecular weight polyethylene -UHMWPE) and a hard counterface (metal or ceramic). For the past 30 years 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. Molecular orientation in biomaterials is thought to be critical in characterizing the precursors of wear and the production of debris during the wear process. Current methods of inferring or deducing orientation are not accurate and often rely on staining and cutting specimens. In this study we use the electric field polarization dependence of soft x-ray absorption to directly determine molecular orientation in UHMWPE and evaluate the utility of this technique for evaluating artificial joint materials. We have measured the change in molecular orientation of ultra high molecular weight polyethylene (UHMWPE) samples subjected to various wear motions and duration. Two motions were used: a unidirectional and a cross-shear (motion to form figure-eight) motion. The observed orientations of the UHMWPE molecular chains using soft x-ray absorption are discussed and contrasted with the current understanding of the wear process in UHMWPE.

11:40am **BI-ThM11 Peptide Functionalized Titanium Alloy Surfaces for Orthopedic and Dental Materials***, **F.A. Akin**, L. Hanley,* University of Illinois, Chicago*; H. Zreiqat, C.R. Howlett,* University of New South Wales, Australia

Surface modification to a biomaterial may improve long term survival of prosthetic devices. The modulation of bone behavior was examined by surface chemical modification of titanium alloy (Ti-6Al-4V) using peptides. RGDSC (arginine-glycine-aspartate-serine-cysteine) was covalently bound to the Ti-6Al-4V surface by 3-aminopropyltriethoxysilane. Surface characterization of amine-, cysteine-, and RGDSC-terminated Ti-6Al-4V was determined using x-ray photoelectron spectroscopy, roughness assesment, and scanning electron microscopy. All elemental peaks as well as the valence band are employed in the x-ray photoelectron spectral analysis of RGDSC on Ti6Al4V. The S(2p) peak was used to determine the atomic percentage of S on the surface, providing information on the peptide surface density. The valence band of the XPS also showed significant differences between the three surfaces. The attachment and proliferation of human bone-derived cell (HBDC) to the amine-, cysteine-, and RGDSC-terminated Ti-6Al-4V were examined using colorimetric and immunohistochemical assays.

Electronic Materials and Processing Division
Room 608 - Session EM1-ThM

Cu, Low-k Dielectrics and Interfaces

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

8:20am **EM1-ThM1 Strength of Nanoscale Copper Under Shear***, P. Heino,* Tampere University of Technology, Finland, FINALND*; P.H. Holloway,* University of Florida*; **E. Ristolainen**,* Tampere University of Technology, Finland

Since 1995 when IBM proposed that copper can be used in electrical interconnections, its properties have received a lot of interest in the electronics community, mainly because of its low electrical resistance. Previously we have shown by comparison with experimental data that mechanical properties of copper can be well described using the effective-medium theory (EMT), molecular dynamics simulations, and more than 100k atoms.@footnote 1@ Here we use these methods to study thermally induced shear strain and stress in several nanoscale copper systems consisting of about 200k atoms. The shear strain in the system is generated by moving the top and bottommost boundaries, corresponding to a common deformation mechanism in flip chip interconnect.@footnote 2@ Plastic deformation mechanisms, stress concentration and stress relaxation were studied. The role of microstructure of the system was analyzed. We studied three monocrystalline systems and several polycrystalline structures, in which the grain size was varied. The results show that the strength of the system decreases with decreasing grain size. This is contrary to macroscale behavior, but has recently been found in similar systems under tension. The reason behind this behavior is the soft grain boundary and grain boundary sliding. The strength of the small systems can decrease by a factor of ten, when the structure changes from monocrystalline to polycrystalline. In monocrystalline structures we studied dislocation formation. The results showed that dislocations prefer to initiate at the compressive side of the system rather than at the tensile side. This peculiar behavior could be exlained with the stacking fault energy and its dependence on the state of strain in the context of EMT. More details will be discussed. @FootnoteText@ @footnote 1@P. Heino, H. Häkkinen and K. Kaski: Europhysics Letters 41 (3) 278 (1998) @footnote 2@P. Heino and E. Ristolainen: Proc. Second Int. Conf. on Modeling and Simulation of Microsystems, Apr. 19-21 (1999), San Juan, PR, USA.

8:40am **EM1-ThM2 A Discussion of the Interconnection Science and Technologies*, S.P. Murarka,*** Rennselaer Polytechnic Institute **INVITED**

Shrinking device dimensions have affected the interconnect performance leading to replacement of Al with Cu and investigations of a variety of low-K materials to replace SiO@sub 2@ and of other modes (e.g. optical) of signal transmissions between devices and devices and the outside world. As the surface-to-volume ratio increases, the surfaces and interfaces will control the properties and reliability of the interconnection and dielectric materials. In this paper, we will review and discuss the science and technology of interconnections for semiconductor circuits and the impact of surfaces and interfaces on their performance.

9:20am **EM1-ThM4 Electrochemical Deposition Cu Films for ULSI Applications*, J.C. Hu,*** National Tsing Hua University, Taiwan, R.O.C.*; T.C. Chang,* National Nano Device Laboratory, Taiwan, R.O.C.*; W.C. Gau, C.L. Cheng,* Chung-Yuan University, Taiwan, R.O.C.*; M.S. Feng,* National Chiao-Tong University, Taiwan, R.O.C.*; Allen Yang, Kevin Lee,* Merck-Kanto Advanced Chemical Ltd., Taiwan, R.O.C.*; L.-J. Chen,* National Tsing Hua University, Taiwan, R.O.C., Republic of China

Cu is being considered to replace aluminium in ULSI circuit metallization for better conductivity, higher electromigration resistance and reliability. CVD and PVD used to deposit Cu layer have been well documented. Relatively little is known about electrochemical deposition method to deposit copper films despite successful applications in ULSI by a number of manufacturers. The additives play a very important role in super-filling behavior. However, most of additives in electoplating solution are not disclosed in the literatures. In the present work, the new additives of electroplating solution without brightening-agents were investigated. The texture of the electroplated Cu films was studied with various applied current densities. A kind of ester was investigated as a leveling-agent. The polyethers were used as surfactants. ECD Cu deposited on low dielectric constant material like hydrogen silsesquioxane (HSQ) was studied. The basic electroplating solution was composed of CuSO@sub 4@.5H@sub 2@O (50-100 g/l), H@sub 2@SO@sub 4@ (150-200 g/l), HCl (50-80 ppm). Patterned wafers were fabricated to examine the ability of gap filling of electroplated Cu. 30-nm-thick TaN films as barriers and 100-nm-thick Cu films as seed layers were deposited by ionized metal plasma (IMP) PVD, respectively. The opening width of trenches/vias was 0.18-0.8 µmm . Applied current densities were less than 1.0 A/dm@super 2@. Transmission electron microscopy and X-ray diffractometry were utilized to investigate the microstructures and crystal orientation. Auger electron spectrocopy was applied to determine the stoichiometry and uniformity along the depth direction. The morphology was studied by a scanning electron microscope. Low resistivity, low porosity, and highly uniform electroplated Cu films were obtained, even without brightening-agent. 0.2 µmm vias and trenches with an aspect ratio of 5 were filled completely without void or seam. The Cu films exhibit a good super-filling behavior. Super-filling behavior can be explained by a diffusion-controlled theory of leveling-agents. The resistivity of a 450-nm-thick Cu film is 1.84 µm@ohm@-cm. From XRD analysis, strong (111) texture was obtained in the electroplated Cu films. The concentration of oxygen in the sample was found to be rather low.

9:40am **EM1-ThM5 Complete Filling of High-Purity Copper in Subquarter-Micron Trench Structure Using Plasma CVD Reactor with H Atom Source*, H.J. Jin,*** *M. Shiratani, Y. Nakatake, K. Koga, T. Kinoshita, Y. Watanabe,* Kyushu University, Japan

Complete filling of high-purity copper in subquarter-micron trench structures is a key requirement in formation of metal interconnects carrying signals in ULSI. For this interconnect application, we have developed a plasma CVD reactor equipped with an H atom source in order to control independently the concentration of H atoms and the degree of dissociation of Cu(hfac)@sub 2@, since H atoms are extremely effective in removing impurities within the film and deposition rate and film conformality presumably depends on the degree of dissociation of Cu(hfac)@sub 2@.@footnote 1,2,3@ High-purity Cu films (about 100%) with the low resistivity of 2 @micro n@@ohm@cm can be deposited, even with the low H@sub 2@ gas volume fraction of 50-67%, by using the H atom source, while high-purity films are obtained only for an H@sub 2@ gas volume fraction above 90% for the CVD reactor without the source. In order to evaluate Cu filling property in trench structures using the plasma CVD reactor with the H atom source, coverage shape of the Cu deposited film in a trench 0.4 µm wide and 3.25 µm deep is examined under conditions for which high-purity (about 100%) Cu films are obtained. While the coverage at the bottom of trench is 0% for the main discharge power P@sub m@ = 80 W, it increases with decreasing P@sub m@ to reach 95% for P@sub m@ = 15 W. These results show that a decrease in P@sub m@ leads to a reduction in the sticking probability of Cu-containing radicals, a low value of which is essential for the achievement of complete filling of extremely small width and high aspect ratio trench structures. We also have succeeded in complete and void free filling in trench 0.3 µm wide and 1 @micron@ deep using such control. Cross sectional TEM observation of Cu films shows that size of Cu grain is above 0.5 µm. @FootnoteText@ @footnote 1@M. Shiratani, et al., J. Phys. D, 29 (1996) 2754. @footnote 2@H. J. Jin, et al., J. Vac. Sci. & Tech. A17 (1999). @footnote 3@H. J. Jin, et al., Jpn. J. Appl. Phys. July (1999).

10:00am **EM1-ThM6 The Stability of Thin TiN and TaN Layers as Diffusion Barriers for Copper under Thermal Annealing and Bias Temperature Stress Conditions***, H. Kizil, G. Kim, **C. Steinbrüchel,*** Rensselaer Polytechnic Institute*; B. Zhao, L. Tsau, M. Brongo,* Conexant Systems

The stability of TiN and TaN as diffusion barriers for Cu has been investigated using capacitance-vs-voltage (C-V) and leakage current-vs-voltage (I-V) measurements as a function of thermal annealing and bias temperature stress (BTS) conditions. Samples consisted of MOS capacitors with a film stack of 300 nm Cu/barrier/25 nm thermal silicon dioxide on Si. The barrier thickness was 5, 10, or 20 nm. Samples were pre-annealed in Ar/3% hydrogen for 30 minutes at various temperatures. BTS treatments were performed at 2 MV/cm and 250 C, 2 MV/cm and 200 C, and at 1.5 MV/cm and 250 C, for periods of up to one hour in flowing nitrogen. The main results can be summarized as follows: In order for BTS to yield negligible flat-band voltage shifts, pre-annealing at 350 C is necessary. This produces a substantial number of initial leakage current failures (i.e. before BTS) with TiN but not with TaN. BTS of samples pre-annealed at lower temperatures causes significant shifts in the C-V plots. However, the flat-band voltage shift (or the absence thereof) is not a very good indicator of barrier stability, in the sense that samples with minimal shifts in the C-V plots may still give unacceptably high leakage currents. TaN consistently behaves better than TiN under all stress conditions.

10:20am **EM1-ThM7 Surface Modification and Cleaning Enhancement of TaSiN Films with Dilute Hydrofluoric Acid****, **P.J.S. Mangat**, W.J. Dauksher, K.D. Cummings,* Motorola, Inc.*; W.L. O'Brien,* Mad City Labs, Inc.

Amorphous TaSiN and TaSi alloys films are of great interest for application in the fabrication of reticles for Next Generation Lithography (NGL) and for incorporation in semiconductor devices. TaSiN films act as absorber and scatterer, respectively, on the masks for X-Ray Lithography and Scattering with Angular Limitation in Projection Electron-beam Lithography. Recently, we have successfully extended its application to an absorber for Extreme Ultra-Violet Lithography reticles. The films have been extensively characterized in terms of resistivity, composition, defectivity, surface roughness, crystalline state, and chemical robustness. One little understood, but critical characteristic of these films, is that they undergo stress change from tensile to compressive upon interaction with dilute Hydrofluoric (HF) acid. We have investigated the cause of this behavior using high-resolution core level (Ta 4f and Si 2p) photoemission spectroscopy with synchrotron radiation. Our results using photoemission and Auger electron spectroscopy confirm that surfaces of as-deposited and annealed films are composed primarily of Si-oxides with trace amounts of Ta-oxide. Upon interaction with HF, the surface oxide undergoes major reorganization and Ta gets heavily oxidized resulting in the formation of Ta2O5. Such a reaction would lead to a build up of strain in the oxidized region, which we interpret as being contributing factor for the observed stress changes in the TaSiN thin films. We further extended the study in terms of desorbtion of the surface oxide. Upon annealing the surface, we observe that the temperature for oxide desorbtion is reduced by 200 oC from 650 oC due to the HF interaction. This can be attributed to a change in the bonding configuration by HF, wherein the Si-O bonds are broken and weak Ta-O bonds are formed. This causes the loosely bonded oxide to desorb at lower temperatures. * Work Performed at Synchrotron Radiation Center,UW-Madison, Stoughton, WI 53589.

10:40am **EM1-ThM8 Fluroinated Amorphous Carbon - A Low Dielectric Constant Material for Multilevel Interconnect Applications***, **W. Zhu**, C.S. Pai, H.E. Bair, H.W. Krautter, B.S. Dennis,* Lucent Technologies **INVITED**

Low dielectric constant (k) materials are key components for the next generation backend-of-the-line interconnect architectures. We investigated the fundamental relationships among the deposition, structure and properties of low k fluorinated amorphous carbon (a-C:F) films. We found that the useful low k a-C:F films need to possess a carbon structure with an optimal amount of crosslinked, sp3 bonded carbon atoms. This dictates that the F/C atomic ratio is in a narrow range of 35-45%, and the films contain no hydrogen. We have successfully deposited robust a-C:F films with k<2.8 and with physical properties meeting stringent requirements for device integration.

11:20am **EM1-ThM10 Multilayered Si-Based Organic Thin Films with Low-Dielectric-Constant Formed by Plasma-Enhanced Chemical Vapor Deposition from Hexamethyldisiloxane***, **M. Okumura**, S. Ichiyanagi, T. Fujii, M. Hiramatsu, M. Nawata,* Meijo University, Japan

As the device geometries of ultralarge scale integration (ULSI) circuits continue to shrink, low-dielectric-constant interlayer dielectric films are required in order to realize ULSI devices of high performance. We have previously reported a remote plasma-enhanced chemical vapor deposition (PECVD) from hexamethyldisiloxane (HMDSO) and O@sub 2@ using a radio-frequency (rf, 13.56MHz) inductively coupled plasma (ICP) source for the formation of Si-based organic thin films as a new insulator with a dielectric constant lower than 3.0. In this work, to improve the thermal stability and dielectric property of Si-based organic thin films fabricated by PECVD with HMDSO, multilayered structure of methyl-siloxane layer and thin silicon-oxide layer has been proposed. After the deposition of the first Si-based organic film using PECVD from HMDSO and O@sub 2@ at room temperature, the film was rapidly annealed by the irradiation of CO@sub 2@ laser beam with exposed to O@sub 2@ plasma without HMDSO in order to transform the surface of the organic film into silicon oxide for the improvement of thermal stability. The second Si-based organic layer was deposited on the transformed layer, and the surface of the top layer was transformed into silicon oxide in the same manner. This procedure was repeated at most 20 times. Chemical compositions and structures of the multilayered films were analyzed by x-ray photoelectron spectroscopy and Fourier transform infrared spectroscopy. The dielectric constant of the multilayered Si-based organic thin films varied from 2.6 to 4.5. The effects of deposition conditions on the film properties were investigated.

11:40am **EM1-ThM11 Low-k Si-O-C-H Composite Films Prepared by Plasma Enhanced Chemical Vapor Deposition using BTMSM(bis-trimethylsilylmethane) Precursor***, **Y.-H. Kim**, H.J. Kim,* Seoul National University, Korea

As the ultra-large scale integrated circuits(ULSI) are shrunk to deep sub-micron dimension, RC signal delay, cross-talk, and power consumption are seriously increased. Therefore, there has been a strong demand for low-k inter-metal dielectric materials instead of the conventional SiO@sub 2@ in order to improve the performance of ULSI devices. Many researchers have proposed various organic and inorganic materials as the substitute for SiO@sub 2@. Among them, silicon oxide-based dielectric materials containing alkyl groups have been attractive alternatives due to their high thermal stability. The steric hindrance of the alkyl groups remains nano-pores in silicon oxide and the dielectric constant is decreased. Therefore, in order to get lower value of dielectric constant, the more alkyl groups have to be included in silicon oxide. However, the over-much alkyl groups could degrade the thermal stability of this material. To achieve good thermal stability as well as the low dielectric constant, we prepared the Si-O-C-H composite films by plasma enhanced chemical vapor deposition using bis-trimethylsilylmethane(BTMSM, H@sub 9@C@sub 3@-Si-CH@sub 2@-Si-C@sub 3@H@sub 9@), which is neither toxic nor flammable. Major feature of this precursor is a very strong Si-CH@sub 2@-Si bond between two silicon atoms, therefore, the Si-O-C-H composite films deposited using BTMSM were expected to have good thermal stability as well as low dielectric constant. To investigate the thermal stability of the Si-O-C-H composite films, FT-IR analysis and capacitance-voltage measurement were carried out before and after heat-treatment. Film morphology and step coverage were examined by the electron microscopy (SEM and TEM).

Electronic Materials and Processing Division
Room 612 - Session EM2-ThM

Dielectric Passivation/Oxides on Compound Semiconductors

Moderator: K.G. Eyink, Air Force Research Laboratory

9:00am **EM2-ThM3 Dielectric Passivation/Oxides on Compound Semiconductors***, **F. Ren**,* University of Florida*; M. Hong,* Bell Laboratories, Lucent Technologies*; S.J. Pearton, C.R. Abernathy, G. Dang,* University of Florida*; J.R. Lothian,* Multiplex Inc. **INVITED**

Electronic and optical devices based on GaAs, InGaAs and GaN material systems have been widely used in telecommunication and wireless communication applications. In order to improve the device performance and reliability, device passivation is one of the critical steps in the device fabrication. An electron cyclotron resonance chemical vapor deposition (ECRCVD) silicon nitride (SiN@sub x@) was successfully demonstrated to passivate submicron T-gate. Combining ECRCVD SiN@sub x@ and an in-situ dielectric film passivation technique by dividing a thick film deposition into many thin film (<40Å) depositions and using a N@sub 2@ ion bombardment between the depositions. A thermally stable (up to 800 °C) SiN@sub x@ was achieved with this process. The refractive index of N@sub 2@ treated SiN@sub x@ film only changed 0.3% when the SiN@sub x@ film was heated up to 1000 °C and the film with a continuous deposition showed a 2.5% change. The etch rates of passivated SiN@sub x@ film in BOE and diluted HF are 40 Å/min which is much slower than that of un-treated SiN@sub x@(135 Å/min). Recently, an in-situ deposition of Ga@sub 2@O@sub 3@(Gd@sub 2@O@sub 3@) on InGaAs, GaAs and GaN has been demonstrated. The Ga@sub 2@O@sub 3@(Gd@sub 2@O@sub 3@)/GaAs interfaces showed a very low interface state densities. Enhancement and depletion mode GaAs metal oxide semiconductor field effect transistors (MOSFETs) have been demonstrated with excellent performance. Enhancement mode InGaAs and depletion mode GaN were also demonstrated.

10:00am **EM2-ThM6 Study of GaAs Oxidation in H@sub 2@O@sub 2@ and H@sub 2@O using Spectroscopic Ellipsometry***, **S.-J. Cho**, P.G. Snyder,* University of Nebraska, Lincoln

Oxidation of GaAs in hydrogen peroxide (H@sub 2@O@sub 2@) and deoinized H@sub 2@O (DH@sub 2@O) at room temperature was studied using in-situ real time spectroscopic ellipsometry (RTSE) and ex-situ spectroscopic ellipsometry (SE). GaAs samples were immersed in H@sub 2@O@sub 2@ for periods of up to 2 hours while RTSE data were recorded, then rinsed in flowing DH@sub 2@O and blown dry. SE data (1.5-5.5 eV) were taken before and after immersion. Analysis of the SE data indicated the development of a 2-3 nm interface (modeled as porous GaAs) between the oxide and GaAs, which was not present before immersion. The oxide itself had also become more porous as well as thicker. Accurate modeling of the interface and oxide layers required data in both the E@sub 2@ (~4-5 eV) and E@sub1@ (~2.5-3.5 eV) spectral regions. The RTSE spectral range was limited to below 3.5 eV by UV absorption in the H@sub 2@O@sub 2@ ambient, so the interface could not be included in the real time analysis. Another problem was the formation of bubbles on the surface, which became visible after about 30 minutes. Within these limitations on the RTSE data, their analysis indicated that the oxide growth was approximately logarithmic over at least the first 10-15 minutes. The oxidation rate varied from 0.21 to 0.54 nm/decade (minutes). In DH@sub 2@O no bubbles formed, but an interface again appeared to be present. Oxidation was nearly linear in time, at a higher rate than in the H@sub 2@O@sub 2@, and with a higher void volume (more porous oxide). Growth rates again varied considerably, with a typical rate 0.16 nm/min. Research supported by AFOSR Grant #49620-96-1-0480.

10:20am **EM2-ThM7 The Effective Two-step Passivation of Metal/GaAs Interface with Sulfur and Hydrogen Plasma***, **M.G. Kang**, J.W. Kim, H.H. Park,* Yonsei University, Korea

In application of GaAs to device integration, the reliable and controllable Schottky contact property of metal/GaAs is urgently necessary to yield. However, it is limited to develop furthermore due to the existence of defects at/near the metal/GaAs interface. In this study, a novel method of passivating the defects with sulfur and hydrogen plasma at/near the metal/GaAs interface was investigated. The sulfur-passivation was employed to passivate the defects at GaAs surface, and the defects in GaAs adjacent to the surface were co-passivated using hydrogen plasma. The native oxide of GaAs was completely removed by the surface treatment using HCl solution. The GaAs surface was then passivated with sulfur in a monolayer thickness using (NH@sub 4@)@sub 2@S@sub x@ solution. After the treatment, the surface could be protected from air-oxidation and preserved oxide-free-surface during a followed metallization. In particular, ultra thin Au metal of 5 nm thickness was deposited on the sulfur-passivated GaAs surface prior to hydrogen plasma treatment, in order to protect the GaAs surface from plasma-induced damage. The defect density of the metal/GaAs interface was greatly reduced by this two-step passivation method, compared to GaAs treated with either sulfur or hydrogen. The defects were evaluated by low temperature photoluminescence and deep level transient spectroscopy. The chemical bonding state of GaAs before and after Au-metallization was characterized using an angle-resolved X-ray photoelectron spectroscopic technique.

10:40am **EM2-ThM8 Advanced Selective Dry Etching of GaAs/AlGaAs in High Density Inductively Coupled Plasmas*, J.W. Lee*,** *M.W. Devre, B.H. Reelfs, D.J. Johnson, J.N. Sasserath,* Plasma-Therm, Inc.*; F. Clayton,* Motorola, Inc.*; S.J. Pearton,* University of Florida

We report a breakthrough for selective etching of GaAs over Al@sub X@Ga@sub 1-X@As, x = 0.2, etching with a high density plasma source. This results is particularly important for III-V devices such as HBTs or HEMTs. For example, fabrication of HBTs requires a process for selective etching of a GaAs contact layer while stopping on AlGaAs layer. Inductively coupled plasma (ICP) etching with BCl@sub 3@/SF@sub 6@/N@sub 2@/He chemistries showed extremely high selectivity of GaAs over AlGaAs (> 200 : 1) and a photoresist (> 10 : 1). This process also produced excellent sidewall passivation on GaAs with reasonablely high rate (> 1500 Å/min.). Both SEM and AFM data showed AlGaAs etch stop layer was quite smooth after processing. We found that He played a key role in enhancing selectivity and obtaining smooth AlGaAs surfaces. When used with resist masks, addition of N@sub 2@ into BCl@sub 3@/SF@sub 6@ plasma helped formation of passivation on the sidewall and maintained high anisotropy. An optimized condition with BCl@sub 3@/SF@sub 6@/N@sub 2@/He ICP plasmas showed excellent pattern transfer into GaAs with high rate, anisotropy and selectivity.

11:00am **EM2-ThM9 Characterization of Hydrogen Passivation in p-type InP (100)*, W.E. Henderson*,** Clark Atlanta University*; M.D. Williams,* Clark Atlanta University, US

Hydrogen in p-type semiconductors acts to passivate (i.e. neutralize) the charge carrier contribution of impurity charge centers by forming acceptor-H+ complexes. We study the passivation of several common p-type dopants in InP (100) including Zn, Be, and Cd. The InP substrates are exposed to atomic hydrogen created by a radio-frequency generated plasma source. Secondary ion mass spectrometry and capacitance-voltage profiling are used to determine the degree of neutralization as a function of depth. This work is supported by the DoE through grant # DE-FG02-97ER45647.

11:20am **EM2-ThM10 Synchrotron Radiation-Induced Wet Processing of GaAs**, Q. Ma*,** *D.C. Mancini, R.A. Rosenberg,* Argonne National Laboratory

To explore the potential for photoelectrochemical processing of materials using hard x-rays generated by a third-generation synchrotron radiation (SR) light source, we initiated studies of SR-induced surface wet etching and metal deposition. We report in this paper a room-temperature, x-ray-induced chemical wet etching process that produces smoothly etched surfaces on n-GaAs using a HNO@sub 3@ solution as the reagent. Atomic force microscope measurements indicate a root-mean-square surface roughness of @<=@ 1.5 nm, which compares favorably to the unetched surface roughness. An etch rate of up to 64 nm/min was achieved under current experimental conditions, which still leaves room for significant enhancement. Dependence of the etching rate on photon intensity, photon energy, semiconductor doping types, and solution concentration, as well as the etched surface chemistry have been studied in order to understand the underlying mechanism. We will also report a preliminary result of patterned wet metal deposition on n-GaAs using a commercial Ni-containing electrolyte and describe the processing. *The submitted manuscript has been created by the University of Chicago as Operator of Argonne National Laboratory ("Argonne") under Contract No. W-31-109-ENG-38 with the U.S. Department of Energy. The U.S. Government retains for itself, and others acting on its behalf, a paid-up, nonexclusive, irrevocable worldwide license in said article to reproduce, prepare derivative works, distribute copies to the public, and perform publicly and display publicly, by or on behalf of the Government.

Magnetic Interfaces and Nanostructures Technical Group Room 618/619 - Session MI+NS-ThM

Patterned or Self-Assembled Magnetic Nanostructures

Moderator: Z.Q. Qiu, University of California, Berkeley

8:20am **MI+NS-ThM1 1-D Propagation of a Magnetic Domain Wall in Submicron Magnetic Wire*, T. Ono,*** *H. Miyajima,* Keio University, Japan*; K. Shigeto, K. Mibu, N. Hosoito, T. Shinjo,* Kyoto University, Japan **INVITED**

A novel method to detect single domain wall motion in a submicron magnetic wire by utilizing the giant magnetoresistance (GMR) effect is presented.@footnote 1@ Recent developments of nanolithography techniques make it possible to prepare submicron dots or wires with well-defined shape, leading to the current attention on the quantum phenomena in mesoscopic magnetic materials, such as macroscopic quantum tunneling and macroscopic quantum coherence. However, the direct magnetization measurements of mesoscopic magnetic materials are practically difficult because of their small volume, and have been performed using samples consisting of a huge number of presumably identical particles. As a result, the essential magnetic properties of a single particle or wire were masked by the inevitable distribution of size or shape. Up to now, quantitative measurements on dynamical properties of a domain wall in a submicron magnetic wire, such as velocity estimation were almost impossible. The method described in this paper has a great advantage to detect a single magnetic domain wall motion, since the GMR change is directly proportional to the magnitude of the switching layer magnetization in a magnetic wire. It should be noticed that the domain wall position can be determined by this method as a function of time, and, thus, we can measure the velocity of a single domain. The wall velocity linearly depends on the applied magnetic field H and is described as v = μ(H - H@sub 0@), where v is the wall velocity, μ so-called wall mobility. In case of NiFe wire 40 nm in thickness and 500 nm in width, it was obtained that μ = 2.6 (m/sOe), and H@sub 0@ = 38 (Oe) at 100 K. @FootnoteText@ @footnote 1@ T. Ono, H. Miyajima, K. Shigeto, K. Mibu, N. Hosoito and T. Shinjo, Science, 284 (1999) 468-470.

9:00am **MI+NS-ThM3 Magnetism of Interconnected Co Nanodots Grown on the N-modified Cu(001) Surface*, K.D. Lee*,** *T. Iimori, F. Komori,* University of Tokyo, Japan

Square arrays of ultrathin Co nano-size dots interconnected by 1 monolayer-height Co nanostripes are grown on the N-modifed Cu(001)c(2x2) substrate. Scanning tunneling microscopy shows the Co atoms are nucleated at the naked Cu(001) substrate exposed between ordered arrays of c(2x2) square patches forming such a novel Co nanostructure. The sizes of Co dots and interconnecting nanostripes are controlled by the amount of Co deposition at room temperature. Magnetic properties of these nanostructures have been investigated by using magento-optical Kerr effect between 100 K and 450 K. Analysis of hysteresis loops as a funtion of temperature as well as thickness reveals that these Co dot arrays have remarkably different magnetic properties from ultrathin fcc Co films grown on clean Cu(001) surface with the same average thickness, such as two-step increase of the saturation magnetization and coercivity with decreasing temperature. We attribute these novel magnetic properties to the magnetic interaction among Co dots mediated by the interconnecting Co stripes.

9:20am **MI+NS-ThM4 Periodic Magnetic Microstructures using Glancing Angle Deposition*, B. Dick*[1],** *M.J. Brett, M. Malac, R.F. Egerton,* University of Alberta, Canada

Arrays of magnetic pillars have been proposed as a potential high-density data storage medium.@footnote 1@ The advanced deposition technique known as GLancing Angle Deposition (GLAD)@footnote 2@ has been used to fabricate Ni and Co posts. Because of the nature of initial film nucleation, these posts were distributed randomly on the substrate surface with a large-scale periodicity of around 350nm and individual post diameters of 100 to 150nm. We have grown arrays of posts by suppressing the randomness inherent within the initial nucleation stage of film growth. Shadowing sites were fabricated by pre-patterning a thin Cr or Ti layer on silicon substrates into a square array using electron beam lithography. These sites shadow regions of the substrate from incident flux during film deposition and act as preferred nucleation sites for the Ni and Co pillars. Using this process, we have obtained a regular post period of 500nm, with post diameters and heights of 300nm and 375nm respectively. This presentation will describe the GLAD deposition process, report on the

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[1] **Falicov Student Award Finalist**

film's periodic structure, and characterise the film's domain structure (MFM) and hysteresis response curve. Further development on decreasing the period between individual posts is continuing, and we exptect that 200nm spacing should be attainable using this simple, single-step evaporation process. @FootnoteText@ @footnote 1@S.Y. Chou. Proceedings of the IEEE. 85(4), 1997. @footnote 2@K. Robbie, J.C. Sit, M.J. Brett. J. Vac. Sci. Technol. B. 16(3), 1998.

9:40am **MI+NS-ThM5 Magnetic Quantum Cellular Automata***, **R.P. Cowburn,*** University of Cambridge, UK, United Kingdom*; D.K. Koltsov, A.O. Adeyeye, M.E. Welland,* University of Cambridge, UK **INVITED**

Nanometre scale magnetic particles (nanomagnets) are promising candidates for implementing Magnetic Quantum Cellular Automata (MQCA) architectures. In order to use nanomagnets in this way their magnetic properties must be fully understood. In particular, the conditions required to obtain a single domain state (and hence the ability to signal a 1 or a 0) must be established. Furthermore, in order to achieve room temperature operation of MQCA, magnetostatic coupling between nanomagnets must be understood and controlled. We have performed a detailed experimental and theoretical investigation into these aspects of nanomagnetism. We have used high resolution electron beam lithography to fabricate nanomagnets in the size range 40-500nm with elliptical or circular geometries. We find that the shape anisotropy introduced by the elliptical form greatly stabilises the single domain state; in the absence of any ellipticity, all of the nanomagnets greater than approximately 100nm in diameter collapse into a flux closing vortex state. We have then fabricated chains of sub-100nm nanomagnets with gaps as small as 15nm between neighbouring edges. We find experimental evidence for strong magnetostatic coupling. We have thus achieved the conditions necessary for a MQCA implementation, i.e. a well defined digital state even at room temperature which can be switched by interactions from neighbouring cells. We have used the finding described above to make a working room temperature MQCA gate. CMOS electronic signals are interfaced directly to the magnetic system by passing a small current through a gold track underneath part of the gate; outputs are currently read by focusing a laser beam onto a magnetic test point and using the magneto-optic Kerr effect to monitor its magnetic state. The gate achieves an overall power gain (and hence the ability to work at room temperature and to fan out) by an applied oscillating magnetic field.

10:20am **MI+NS-ThM7 Growth, Magnetization, and Magnetoresistance of Self-Assembled Lateral Multilayers***, E.D. Tober,* Lawrence Berkeley National Laboratory*; **R.F. Marks**, D.D. Chambliss, R.F.C. Farrow,* IBM Almaden Research Center

The angular dependent magnetoresistance, magnetization, and growth of epitaxial Fe@sub eta@Ag@sub 1 - eta@ self-assembled lateral multilayers@footnote 1@ (SALMs)have been examined via MOKE, 4-point resistance probes, STM, LEED, X-ray MCD, and TEM. SALMs consist of epitaxial thin film alloys of immiscible metals grown on Mo(110)/Al@sub 2@O@sub 3@(11-20) template layers and display a unique form of compositional ordering not observed in the bulk. These systems are observed to form a compositionally ordered alloy of alternating, contiguous stripes of Fe and Ag with the long axis of the stripe coinciding with the Mo[001] direction in the plane of the substrate. The average stripe periodicities are on the order of 1.8 to 2.3 nm along the Mo[-110] (perpendicular to the stripes) direction depending on film stoichiometry. These films are found to contain a high degree of magnetic anisotropy with the easy direction lying in-plane parallel to the Mo[001] direction. The low temperature anisotropic magnetoresistance (AMR) and low field magnetoresistance (MR) are examined as a function of field angle for two nearly orthogonal current directions. The SALM structures are observed to display a significant AMR (roughly 10% maximum for the entire structure). Furthermore, a pronounced MR is observed with a maximum @Delta@R/R of 0.88% (~29% in the active layer) at 2.7 K. @FootnoteText@ @footnote 1@ "Self-assembled lateral multilayers from thin film alloys of immiscible metals", E. D. Tober, R. Farrow, R. Marks, K. Kalki, G. Witte, and D. D. Chambliss, Phys. Rev. Lett. 81 N9, 1897.

10:40am **MI+NS-ThM8 Stripe Domains in Ultraflat Fe/Cu(001) Particles***, **C. Stamm**, A. Vaterlaus, U. Maier, D. Pescia,* ETH Zuerich, Switzerland

Atomically thin particles of Fe on Cu(001), grown at room temperature, are investigated using a Scanning Electron Microscope with Polarization Analysis (SEMPA): a Mott detector is used to analyze the perpendicular as well as one of the in-plane spin components of the secondary electrons. The magnetic particles with thickness of a few atomic layers are produced by Molecular Beam Epitaxy through a mask placed in front of the Cu substrate. As in laterally extended thin films of Fe/Cu(001), particles whose lateral size exceed 1 µm contain stripe domains with magnetization perpendicular to the film plane. The width of the stripes is independent of the lateral size of the particles and their shape. Sizing down the Fe particle leads to a single-domain configuration. In contrast, in-plane magnetized ultrathin Co/Cu(001) particles are found in a single domain state, irrespective of their lateral size.@footnote 1@ @FootnoteText@ @footnote 1@C. Stamm, F. Marty, A. Vaterlaus, V. Weich, S. Egger, U. Maier, U. Ramsperger, H. Fuhrmann and D. Pescia, Science 282, 449 (1998).

11:00am **MI+NS-ThM9 Magnetic Properties of Iron Clusters Deposited on Graphite***, **A. Rosén**, M. Andersson,* Göteborg University, Sweden*; M. Hansson,* Chalmers University of Technology, Sweden*; R. Wäppling, B. Kalska,* Uppsala University, Sweden*; N. Tarras-Wahlberg,* Göteborg University, Sweden*; C. Johansson,* Chalmers University of Technology, Sweden

Magnetic properties of iron clusters deposited on graphite Iron clusters with a wide size distribution were produced in a laser vaporisation source and deposited on a graphite substrate. The magnetic relaxation of the clusters was studied with Mössbauer spectroscopy. At 300 K the sample was dominated by fast superparamagnetic behaviour, whereas the relaxation slowed down at lower temperature and six-peak components, representative for static or near-static spinconfigurations, dominated the Mössbauer spectra at 5 K. This indicates that the sample consists of mono-domain particles having an average size between 5 and 10 nm. From the hysteresis loops we obtained that the saturation magnetization was in the range of bulk a -iron and that the coercivity and the remanence increase with decreasing temperature in the whole temperature range. This behaviour is typical for a system of mono-domain particles with a wide size distribution.

11:20am **MI+NS-ThM10 Magnetic Properties of Co and Fe Particles on Sapphire Single Crystal Surfaces***, **T. Risse**, T. Hill, M. Mozaffari-Afshar, H.-J. Freund,* Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany

We have used in situ Ferromagnetic Resonance (FMR) to investigate the magnetic properties of small Co and Fe particles deposited on sapphire single crystal surfaces. Co and Fe grow as 3-dimensional particles, as deduced from the angular dependence of the FMR spectra. This result was confirmed by STM studies on an Al@sub 2@O@sub 3@ model surface grown on top of a NiAl(110) single crystal. The FMR spectra of Co or Fe particles deposited at 298 K reveal a uniaxial out-of-plane magnetization with the magnetization lying in the surface plane. A comparison of the measured angular dependence of the resonance position with 2-dimensional films show that experimental results are consistent with a 3-dimensional growth of the particles determined by the STM measurements. A closer examination of the FMR spectra indicates that these small particles exhibit superparamagnetism. With increasing amount of deposited metal the anisotropy of the systems increases indicating a more ferromagnetic behavior of the system. Annealing the samples to elevated temperatures (900K) leads to structural changes of the particles namely an increase of the particle size as deduced from FMR and Auger spectroscopy. Whereas the qualitative behavior of the magnetic anisotropy for Co deposits remains unchanged, the behavior of the iron particles changes drastically. The particles do not show a uniaxial anisotropy of a single resonance line but a complex pattern of several resonance lines. A discussion of this aspects in terms of shape as well as magnetocrystalline anisotropy will be given. Temperature dependent measurements of the Fe particles reveal a reduced Curie temperature compared to the bulk. The strong changes of the line shape with increasing temperature will be discussed in terms of a thermal fluctuations of the magnetization.

11:40am **MI+NS-ThM11 Magnetic Behavior of Nanosize Cobalt Particles in (SiO@sub 2@, MgO, CoO) Matrix***, **J.Y. Yi**, M.L. Rudee,* University of California at San Diego

Magnetic granular composite films composed of nanosize metal particles separated by a non-magnetic matrix, have interesting magnetic properties due to the finite size of the metal particles. Recently we found that ferromagnetic (FM) and antiferromagnetic (AFM) composite films such as Co-CoO films had much larger coercivity (~1 kOe at 300 K) than conventional granular Co-SiO@sub 2@ films (superparamagnetic at 300 K) in the same composition range. The increased coercivity was believed to be due to the exchange coupling between FM Co and AFM CoO, and the microstructure of the Co particles. These results indicated that the overall properties of the metal phase were affected by not only the intrinsic properties of them but also the characteristics of the matrix phase. To examine the matrix effects, Co-SiO@sub 2@, Co-MgO and Co-CoO granular composite films were prepared by co-sputtering from separate Co and each oxide target. Each film had 30~40 volume % of Co. The estimated Co particle size from x-ray peak broadening effect was about 7 nm. Magnetic hysteresis loops showed that the superparamagnetic behavior of Co at room temperature in the Co-SiO@sub 2@ and the Co-MgO systems whereas 500 ~ 1000 Oe of coercivities were observed in the Co-CoO films. AT 10 K the coercivity of the Co-SiO@sub 2@ film increased to 760 Oe while the coercivity of the Co-MgO and Co-CoO films increased to 6 kOe and 10 kOe, respectively. Unlike the Co-SiO@sub 2@ system, a small M-H loop shift was observed in the Co-MgO system at 10 K and disappeared above 50 K. This results indicated that there would be a small amounts of Co oxide phase existed in Co-MgO films and this may be the reason for the high coercivity at low temperature. In the Co-CoO system, the loop shifts were observed up to 250 K. In this presentation the magnetic properties of each film will be discussed based on the microstructural and magnetic effects from the different matrix.

The Science of Micro-Electro-Mechanical Systems Topical Conference
Room 620 - Session MM+MI-ThM
Processing and Integration Technology

Moderator: L.M. Miller, Jet Propulsion Laboratory

9:00am **MM+MI-ThM3 Magnetic Micromachining Technology: From Materials to Components to Actuators***, M.G. Allen,* Georgia Institute of Technology **INVITED**

The fabrication of micromachined structures based on magnetic elements requires the development of both magnetically soft and hard materials, as well as suitable processes that allow the incorporation of these materials into microelectromechanial systems (MEMS). This presentation summarizes approaches to materials and fabrication techniques for magnetic MEMS, and illustrates their use through several examples, including: flux concentrators to improve the sensitivity of magnetotransistors; integrated inductive components for electronic packages; and fully-integrated, magnetically-actuated microrelays.

10:20am **MM+MI-ThM7 Fabrication and Characterization of Polycrystalline Silicon Thin Films with Hydrofluoric Acid Permeability for Sacrificial Etching of Underlying Oxide Layers***, **Y. Kageyama**, T. Tsuchiya, H. Funabashi, J. Sakata,* Toyota Central R&D Labs., Inc., Japan

Polycrystalline silicon (poly-Si) thin films with permeability to a concentrated hydrofluoric acid solution were fabricated for use in in-situ vacuum encapsulation of micro sensor devices on silicon wafers, and porous microstructures of the films related to the permeability were elucidated. A partial cavitation of grain boundaries, which was induced by heavy doping of phosphorus and consequent segregation of soluble precipitates, was designed for passage of fluid which resolves underlying borophosphosilicate glass (BPSG) or non-doped silica glass (NSG) layer. Poly-Si films of 0.1µm in thickness were made by solid phase crystallization of amorphous films deposited by low-pressure chemical vapor deposition, and were converted to be permeable by doping. Three types of the doping methods were tried, and only a phosphorus oxichloride decomposition method proved to be effective to obtain permeability. The permeability was evaluated by measuring selective removal rates of underlying sacrificial oxide layers, and lateral BPSG removal of more than 50µm was observed within 90 sec at a room temperature through the permeable poly-Si thin films. The removal rates of BPSG layers were about ten times faster than those of NSG layers, which can be attributed to phosphorus concentration in oxide, and were dependent on post-annealing temperatures, whereas those of NSG layers did not depend on the annealing temperatures. The microstructures of these permeable poly-Si thin films were first observed by secondary electron microscope and field emission secondary electron microscope, which revealed submicron pores between silicon grains that acted as the fluid paths.

10:40am **MM+MI-ThM8 A New Chemistry for Rapid Etching of SiO@sub2@***, **C.I.H. Ashby**, C.M. Matzke, L. Griego,* Sandia National Laboratories

Plasma etching of SiO@sub2@ has traditionally been achieved using a fluorocarbon-based plasma. Very fast SiO@sub2@ etch rates (> 1 µm/min) are obtained using high-density plasmas and CH@subx@F@suby@ source gases. Although these plasmas provide fast preferential etching of SiO@sub2@ vs. Si by controlled deposition of a polymer, that same polymer deposition makes CH@subx@F@suby@ processes unsuitable for applications where the surface chemical properties of the SiO@sub2@ are important. Fabrication of deep trenches in fused SiO@sub2@ without chemical alteration of the SiO@sub2@ surface by a fluoropolymer deposit is essential for applications such as electrophoretic and electro-osmotic separations using microfabricated channels ("chemlab on a chip"). Rapid (0.4 µm/min) etching of fused silica has been achieved without the use of polymerizing fluorocarbon gases by the addition of N@sub2@ to SF@sub6@/Ar mixtures in an electron-cyclotron-resonance (ECR) reactor. Addition of N@sub2@ to SF@sub6@ increases the etch rate of SiO@sub2@ by up to 30%. After deep (10 µm) trench etching, the smoothness of the etched surface is comparable to that of unetched SiO@sub2@. Nitrogen might play two roles in enhancing SiO@sub2@ etching: 1) increasing the F atom concentration and/or 2) facilitating the etching of the SiO@sub2@ matrix through the formation of volatile NO@subx@ products. Optical emission studies using Ar actinometry suggest the second mechanism dominates under our plasma conditions. Process characteristics under a variety of plasma conditions 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-AC04-94AL85000.

11:00am **MM+MI-ThM9 Residual Stress Characterization of Thick PECVD Oxide Films for MEMS Applications***, **R. Ghodssi**, X. Zhang, K.-S. Chen, K.A. Lohner, M. Spearing, M.A. Schmidt,* Massachusetts Institute of Technology

Vapor deposited films are of vital importance in many sensors and actuators where they are used to form electrical or mechanical elements. In order to achieve higher electrical and mechanical power levels, thicker films are often desired. However, the deleterious effects of residual stress tend to increase with film thickness. In particular, excessive wafer bow and even cracking may prohibit integration within a micro-device. This paper presents residual stress characterization for PECVD Novellus@super TM@ oxide films with thicknesses in the range of 10 - 40 µm. These films are deposited at 400°C and densified at 1100°C in a nitrogen environment. Wafer curvature measurements were performed to investigate the residual stress in the thick PECVD oxide films as a function of temperature. These results show that the residual stress in thick PECVD oxide films is a combination of both thermal expansion mismatch stress and an intrinsic stress due to the deposition process and resulting microstructure. Furthermore, the densification step plays an important role in determining the residual stress state. For instance, a 10 µm thick PECVD oxide film exhibits a wafer bow of 50 µm and 250 µm before and after densification, respectively. Additional high temperature experiments indicated that cracks formed at temperatures between deposition and densification. The tendency to form cracks is a strong function of film thickness. For films thicker than 15 µm, cracks formed in the film at temperature below 1100°C. Laminated plate theory has been applied to extract residual stress data for the curvature measurements. This data is then correlated with the deposition and densification conditions to guide process development so as to reduce wafer curvature and to eliminate cracking.

11:20am **MM+MI-ThM10 Process and Fabrication of a Thin Film PZT Pressure Sensor***, **E. Zakar**, M. Dubey, B. Piekarski, J. Conrad, R. Piekarz, R. Widuta,* Army Research Lab

Piezoelectric crystals or ceramics are very attractive for static and dynamic pressure sensors. One of the very promising piezoelectric materials is PZT (Lead Zirconate Titinate - 52/48). MEMS technology was applied to fabricate several static PZT pressure sensors and capacitance method was used to characterize it. Sol-gel derived PZT thin films (250 - 500 nm) were deposited on platinized (SiO@sub 2@- 1000/ Ti - 20/ Pt - 170 nm) Si substrates. Top Pt electrode was sputtered deposited on PZT films and was patterned using ion milling. The PZT films were etched using Reactive Ion Etching (RIE) and ion milling. Comparative studies (etched surface, sidewalls and electrical properties) of ion milling and RIE of PZT and oxide were also completed. The RI etch rate of PZT was studied using different electrode shield (graphite, alumina, ardel) materials with power (100 to 500 W) and pressure of HC@sub 2@ClF@sub 4@ gas plasma. The measured RI etch rate of PZT varied from 10-100 nm/min. The ion-milling rate of Pt was 33nm/min, PZT-23nm/min and Oxide-31nm/min. A unique technique of soft and hard bake of photo resists along with change in incidence angles of ion beam were used to eliminate fencing problem during ion milling. Desired slope of the etched walls was also produced using above technique. The etched surface and side walls were smooth and clean up to 2µm feature size. Four level photo-mask process was used to fabricate the pressure sensors. A low stress PECVD oxide film was deposited (at 200°C) to isolate the top and bottom electrodes. The Pt electrodes further bonded with Ti/Au leads which were patterned using wet etching (KOH + I@sub 2@). Several pressure sensors with different dimensions (300x300 and 200x200 µm@super 2@) were fabricated. The average values of measured capacitance, 1023 and 453 pF, are in excellent agreement with calculated values.

11:40am **MM+MI-ThM11 Microfabricated Low-Power Broad-Band Light Source Utilizing Tungsten Filaments***, E.W. Jones, T. George,* JPL-California Institute of Technology*; M.L. Tuma,* NASA-Glenn Research Center*; R. Hansler,* Lighting Innovations-John Carroll University

A miniature,Si chip-based, incandescent light source utilizing tungsten filaments is being developed for integration into fiber optic systems to wavelength multiplex a suite of fiber-optic sensors operating in harsh environments from -50 C to 600 C. The requirements for the light source are that it operate at 2800 K, with an output power >100 mW in the 500-900 nm spectral band with spectral power variance of no more than 4% over the spectral band. In addition, it should be rugged, long-lived, with an output stabilization time of about 1 second, and have a "footprint" comparable to LED devices. Other uses for these filaments are automobile headlights, and systems for vehicle navigation, in remote applications such as monitoring bridges for stress, and industial plant monitoring. To date, several filament fabrication approaches are being attempted. The first uses sputtered tungsten films (1-2 microns thick) patterned in various filament geometries. These filaments have been operated at < 2200 C) is the mounting of coiled-coil wire filaments on microfabricated Si chips. Lastly, 25-micron-thick W sheet stock is being patterned to produce planar spiral filaments. Filaments satisfying the above criteria will be packaged into a hermetically sealed three-chip stack consisting of a bottom reflector chip, a middle filament chip, and a top 5 mm x 5 mm SiN membrane optical window chip, integrated with an optical fiber. The fabrication procedures as well as the optical and electrical characterization results will be discussed in detail.

Manufacturing Science and Technology Group
Room 611 - Session MS+PS-ThM

Environmentally Benign Manufacturing

Moderator: F. Shadman, University of Arizona

8:20am **MS+PS-ThM1 ESH as One of the Key Criteria for Semiconductor Process Development***, A. Bowling, T. Wooldridge, J. DeGenova, T. Yeakley, T. Gilliland, A. Cheng, L. Moyer,* Texas Instruments Inc. **INVITED**

During the development of advanced semiconductor devices, great benefit has been observed by treating ESH as a key process development specification. Earlier it had been feared that one must sacrifice process performance and/or cost to pursue ESH goals. However, in actuality, the process development engineer has frequently found that a process optimized for ESH also has better performance and lower cost per wafer. This paper will give a number of examples where ESH optimization has produced such performance and cost benefits. These examples include DI-water recycling, dilute SC1 wafer cleaning, wafer rinse optimization, dilute HMDS for resist develop, plasma-enhanced chemical vapor deposition (CVD) chamber cleaning optimization of PFC emissions, capture and recycling of copper plating solutions, copper CVD precursor recovery and recycling, post-metal etch solvent clean optimization, vacuum pump oil reclamation/optimization, and IPA recovery and recycling. The paper will conclude that ESH should be treated as another process performance and cost variable just like etch/deposition rate, non-uniformity, and particle counts.

9:00am **MS+PS-ThM3 The Environmental Impact of Perfluorinated Compounds used in the Semiconductor Industry***, R.F. Jewett,* Litmas Corp. **INVITED**

Perfluorinated compounds such as CF@sub 4@, C@sub 2@F@sub 6@, CHF@sub 3@, and others serve as low-toxicity carriers of fluorine for various semiconductor manufacturing processes. The low-toxicity of these chemically stable compounds make the workplace safer, but are a cause of concern when considering their long-term environmental impact. Most PFC's are strong absorbers of infrared radiation. This heat retention, combined with an extremely long atmospheric lifetime makes the environmental impact of continued emission significant and deserving of attention. This paper summarizes the current state of research on the roles of PFC's in the environment, and briefly considers various treatment methods that reduce emissions. There are several commercial systems available which have demonstrated dramatic performance in reducing PFC emissions.

9:40am **MS+PS-ThM5 Optimization of Processing Plasmas in the Semiconductor Industry for Minimal Environmental Impact***, J.G. Langan,* Air Products and Chemicals, Inc. **INVITED**

Most processing plasmas used by the semiconductor industry today have been extensively optimized for manufacturing performance. However, this optimization has traditionally not considered environmental impact as part of the performance criteria. Recent measurements have revealed that essentially all processing plasmas emit some form of gaseous by-products or un-reacted source materials which can be categorized as either volatile organic compounds (VOCs), hazardous air pollutants (HAPs), or perfluorinated compounds (PFCs). Although effective abatement solutions exist for some of these compounds they often transfer the problem from one phase to another requiring subsequent treatment. In an effort to develop truly optimized plasma processes we have investigated the operation of high pressure fluorinated gas (NF@sub 3@, C@sub 2@F@sub 6@) plasmas, predominantly used for CVD chamber cleaning applications, to determine which conditions lead to the highest throughput, lowest environmental impact processes. Using a variety of diagnostics; mass spectrometry, FTIR, electrical impedance analysis, and incident ion energy analysis the effect of operating conditions on etch rate, source gas utilization, by-product formation, and positive ion energy distribution functions have been determined. Using the insight gained from these measurements effective strategies have been identified to maximize the performance of CVD chamber cleans while minimizing their environmental impact. This presentation will give an overview of the environmental challenges associated with gaseous emissions from these tools and our efforts to identify viable solutions for chamber cleans in particular and semiconductor processing plasmas in general.

10:20am **MS+PS-ThM7 PFC Abatement in Inductively Coupled Plasma Reactors using O@sub 2@, H@sub 2@ and H@sub 2@O as Additive Gases@footnote 1@***, X. Xu, M.J. Kushner,* University of Illinois, Urbana

Perfluorinated compounds (PFCs), gases which have large global warming potentials, are widely used in plasma processing for etching and chamber cleaning. Due to under-utilization of the feedstock gases or by-product generation, it is usually necessary to abate emissions of PFCs from plasma processing reactors. Plasma abatement is being developed as one remediation strategy. Previous studies have shown that plasma abatement of, for example, C@sub 2@F@sub 6@ using O@sub 2@ as an additive may be effective in remediating the C@sub 2@F@sub 6@ but may also generate PFC products such as CF@sub 4@. Alternate additive gases may, however, avoid this problem. In this study, the scaling of plasma abatement is investigated using the 2-dimensional Hybrid Plasma Equipment Model (HPEM). Both the plasma etching chamber and downstream plasma burn-box are simulated in order to have realistic entry conditions for the burn-box. O@sub 2@, H@sub 2@, and H@sub 2@O are examined as additive gases in the burn-box. All PFCs in the effluent can generally be remediated in the burn-box at high power deposition with a sufficiently large flow of additive gases. In general CF@sub 4@ generation occurs during abatement of C@sub 2@F@sub 6@ using O@sub 2@ as an additive. CF@sub 4@ is not, however, substantially produced when H@sub 2@ or H@sub 2@O are used as additives due to the consumption of free fluorine by H, OH and H@sub 2@. The end products are dominated by COF@sub x@ with O@sub 2@ and by HF with H@sub 2@. The efficiency of PFC abatement (as measured by eV/molecule abated) decreases with increasing power and decreasing additive mole fraction. @FootnoteText@ @footnote 1@This work was supported by SRC and Applied Materials.

10:40am **MS+PS-ThM8 Modeling of Nonisothermal, Coupled Neutral/Plasma Dynamics in PFC Abatement Plasmas***, M.W. Kiehlbauch, A. Fiala, E.J. Tonnis, D.B. Graves,* University of California, Berkeley

Reducing PFC emissions is an area of increasing concern in semiconductor manufacture. One method of PFC emission reduction is through the use of point-of-use (POU) plasma abatement. In POU plasma abatement, an oxidizing species such as O@sub 2@ or H@sub 2@0 is added to the process tool effluent in the tool foreline. A plasma in the foreline is then used to convert PFCs to oxidized, wet-scrubbable species. Abatement plasmas can be used to reduce PFC emissions from oxide etch and in-situ CVD chamber clean processes and several commercial tools have been designed for these applications. Additionally, the abatement plasma structure is similar to downstream plasma sources which are increasingly used in chemical downstream etch and remote CVD chamber clean. A two-dimensional, coupled plasma and neutral model has been developed and applied to CF4/O2 and C2F6/O2 POU plasma abatement. The neutral model solves the overall neutral mass, momentum and energy balances. Additionally, the species mass balances are solved, together with a rigorous multi-component diffusion formulation. The neutral model is coupled via collisional terms to an INDUCT95 plasma model. The model allows the resolution of neutral temperature profiles and species concentration profiles. At high plasma powers, the neutral mean molecular weight decreases by ~ 50% while the neutral temperature increases by ~ 400%. The resulting density and velocity gradients have a major impact on the plasma structure and the composition of the gas flow leaving the plasma zone. We will present results that show these effects for various PFCs, power deposition profiles, flow rates, pressures and plasma powers. The relative importance of advective and diffusive transport will be considered. Additionally, the effect of wall temperature on the plasma structure will be investigated. Model results will be compared to those obtained experimentally. The application of these results to downstream plasma sources will be discussed.

11:00am **MS+PS-ThM9 Remote Plasma Sources for Cleaning CVD Reactors: Development and Implementation of a Technology for Green Manufacturing of Integrated Circuits***, **S. Raoux**, M. Sarfaty, T. Nowak, K.C. Lai, H.T. Nguyen, S. Thurwachter, J. Schoening, D. Silvetti, M. Barnes,* Applied Materials

The semiconductor industry is pursuing efforts to reduce emission of global warming PFC gases. Recently, a major advance in dielectric CVD (chemical vapor deposition) chamber cleaning has been introduced that virtually eliminates PFCs emissions from the process. Using NF@sub 3@ gas in a remote plasma source, the near complete dissociation of the gas achieves both superior chamber cleaning performance and improved environmental friendliness. In this paper, we will present experimental data (Mass and IR spectroscopy, Optical Emission Spectroscopy) used to identify the major phenomena related to the destruction of NF3 molecules, the generation of reactive (F) species, the recombination of atomic fluorine into F2 molecules and the efficiency of (SiO2, SiN,...) deposition residue removal. We will review the design requirements for this Remote Clean@super TM@ technology with respect to environmental and process performance, manufacturability, integration to the CVD process tool, and energy efficiency. An environmental (EnV) analysis was conducted, based on a process architecture framework, manufacturing process modeling, and multi-dimensional characterization. The EnV analysis integrates ESH impacts, manufacturing costs, and process performance measurements into a larger systems view with dynamic process models, established business processes, and an upstream design approach. The analysis methodology is presented along with a case study to compare an in situ C2F6-based RF clean with the Remote Clean@super TM@ technology.

11:20am **MS+PS-ThM10 Study of NF@sub 3@-Based High Density Plasma Oxide Etch Processes for Reduced Global Warming Emissions***, **L.C. Pruette**, S.M. Karecki, R. Chatterjee, R. Reif,* Massachusetts Institute of Technology

Current oxide etch processes in the semiconductor industry rely on fluorocarbon chemistries, particularly perfluorocarbons (PFCs). The emission of PFCs from these processes has become a cause of concern to the industry because of the long atmospheric lifetimes and the suspected global warming properties of these molecules. Whereas it has been seen that the use of some fluorocarbon molecules in place of PFCs does lead to measurable emissions reductions, stemming typically from a more efficient breakdown in the plasma that that seen with PFCs, it is also known that any process based on a fluorocarbon source material, whether a PFC or not, is likely to emit significant quantities of CF@sub 4@, an extremely long-lived molecule possessing an appreciable global warming potential. The goal of the research presented here is to minimize the amount of CF@sub 4@ and other PFC by-products produced in high density plasma (HDP) oxide etch processes by replacing the fluorocarbon etch gas with an inorganic molecule, namely NF@sub 3@. The NF@sub 3@ gas acts as a fluorine source for the plasma, and is mixed with a rare gas diluent to enhance plasma stability. Experiments illustrating the etch behavior of this dilute NF@sub 3@ plasma with the addition of several different hydrocarbon additives meant to enhance photoresist selectivity and sidewall passivation, and scavenge free fluorine, will be discussed. Scanning electron micrographs (SEMs) will be shown to demonstrate process feasibility. In-situ optical emission spectroscopy data will be used to characterize the plasma, and quadrupole mass spectrometry (QMS) and Fourier-transform infrared (FTIR) spectroscopy data will be used to identify the global warming compounds and hazardous air pollutants (HAPs) found in the process effluent.

11:40am **MS+PS-ThM11 Environmentally Harmonized Silicon Oxide Selective Etching Process Employing Novel Radical Injection Technique***, **K. Fujita**[1], S. Kobayashi, M. Hori, T. Goto,* Nagoya University, Japan*; M. Ito,* Wakayama University, Japan

Dry etching of silicon oxide (SiO@sub 2@) films is an essential process for fabricating deep contact holes in ultra large-scale integrated circuits (ULSIs). This process has been developed by using high-density plasmas employing stable fluorocarbon feed gases such as CF@sub 4@, C@sub 4@F@sub 8@ and so on. Fluorocarbon gases, however, cause a serious environmental problem, namely global warming and hereby the production of fluorocarbon gases would be restricted. Recently, we proposed a novel radical injection technique using a fluorocarbon radical source replacing stable fluorocarbon feed gases for preventing global warming, where polytetrafluoroethylene (PTFE) is ablated by a CO@sub 2@ laser and the generated fluorocarbon species (C@sub x@F@sub y@) such as reactive radicals are injected into the plasma reactor from externally. This technique, therefore, enables us to achieve a new plasma chemistry and a high-efficiency abatement due to the high exhaustion efficiency of reactive radicals coming from the plasma reactor compared with the stable gases. In this study, this system has been successfully applied to high-density plasma etching of SiO@sub 2@ over Si process and CF@sub x@ (x=1-3) radical densities in the plasma were evaluated by infrared diode laser absorption spectroscopy (IRLAS). A permanent magnet ECR plasma source which is very compact in size and easily scaled up to the large wafer size (~30 mm@phi@) was employed. The ECR zone was set about 6.5 cm above substrates. The Etching rate of SiO@sub 2@ and selectivity (SiO@sub 2@/Si) were 650 nm/min and 8, respectively at a microwave power of 400 W, a pressure of 6.5 Pa, a flow rate of 80 sccm and a bias voltage of -450 V in the ECR plasma employing the novel radical injection technique. These results indicate good characteristics compared with the conventional electromagnet ECR plasma. The etching mechanism are discussed on the basis of the behaviors of CF@sub x@ (x=1-3) radicals measured by the IRLAS.

Topical Conference on Emerging Opportunities and Issues in Nanotubes and Nanoelectronics

Room 6C - Session NT+NS+EM+MS-ThM

Nanotubes: Nanoelectronics and Field Emission

Moderator: N.J. Halas, Rice University

8:20am **NT+NS+EM+MS-ThM1 Carbon Nanotube Molecular Electronics***, **C. Dekker**,* Delft University of Technology, The Netherlands **INVITED**

I will present various recent results from electron transport measurements and scanning-probe microscopy on individual single-wall carbon nanotubes. Our early electrical transport work showed mesoscopic signatures at cryogenic temperatures. Additionally, a room-temperature transistor based on an individual semiconducting nanotube was established. Recent results in transport studies include first measurements on samples with low-ohmic contacts. The nanotubes are found to sustain very high current densities (~10^9 A/cm^2). I will show first measurements on kinked nanotubes, which act as an ontube intramolecular junctions. If time allows I may also present our results on AFM manipulation of nanotubes, and electrical measurements on manipulated nanotubes.

9:00am **NT+NS+EM+MS-ThM3 Electrical Transport in Single-Wall Nanotube Rings: Coherence and Localization***, H.R. Shea, R. Martel, **Ph. Avouris**,* IBM T.J. Watson Research Center

Understanding electrical transport in carbon nanotubes is essential for their possible use in nanoelectronics. Furthermore single-walled carbon nanotubes (SWNTs) provide ideal model systems on which to test theories of transport phenomena in 1D-systems. Linear SWNTs, however, do not have self-folding electron trajectories which can enclose magnetic flux. Thus, the technique of magneto-resistance (MR) cannot be applied directly to obtain information on the mechanism of electrical transport. Recently, we have developed a procedure by which linear SWNTs can be induced to form ring structures. Despite the high flexural rigidity of these materials, coils stabilized only by van der Waals forces can be produced in yields of ~50 %. These rings provide an ideal geometry for MR measurements. The MR is negative over the range of 0-5 T and from it we are able to determine the coherence length of the electrons in the rings. We found that over the entire range of 3 K - 60 K the SWNT-rings are in a state of weak localization

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

induced by the constructive interference of electron waves propagating in opposite directions around the ring. Electric transport is not ballistic, and the coherence length reaches 520 nm at 3 K. From the temperature dependence of the coherence length we determine that the dominant dephasing mechanism at low T involves electron-electron interactions (Nyquist mechanism). Below ~1 K we observe an electronic phase transition to a strongly localized state. This transition is accompanied by the opening of a small energy gap and very strong MR and universal conductance fluctuations. An interesting zero bias anomaly (ZBA) is also observed below ~0.7 K. This ZBA is sensitive to magnetic fields and is ascribed to Kondo-type scattering from localized magnetic moments.

9:20am **NT+NS+EM+MS-ThM4 Analysis of Carbon Nanotube Field-Effect-Transistors (FETs)*, T. Yamada,*** NASA Ames Research Center

Recent experiments on carbon nanotube FETs@footnote 1@ are analyzed theoretically. Comparing to the familiar Metal-oxide-semiconductor (MOS) FET characteristics, two qualitatively different behaviors can be pointed out:@footnote 1@ (1) the channel conductance g@sub d@ as a function of gate voltage V@sub g@ is not linear but somehow saturates, and (2) the drain current I@sub d@ does not saturate with the drain voltage V@sub d@ but rather monotonically increases. As for g@sub d@(V@sub g@), a staircase-like curve is expected with possible rounding. Each time the Fermi energy crosses a degenerate new subband, the nanotube conductance increases by double the quantum conductance, and thus g@sub d@ forms steps. When moving up to a next step, one new additional degenerate subband needs to be filled in the inversion layer, where larger V@sub g@ has to be applied. This will be a mechanism for the g@sub d@ saturation. The absence of I@sub d@(V@sub d@) saturation is due to the infrequent inelastic scattering by phonons or other carriers in the channel, regardless of the frequent elastic scattering by defects or impurities determining the small g@sub d@ (1/g@sub d@ ~ 2.9 M@ohm@).@footnote 1@ Carriers are not thermalized in the channel without efficient inelastic scattering, resulting in no channel pinch-off formation and no I@sub d@ saturation. These reflect the nanotube electronic properties. We need to take them into account in the future device/circuit design, and develop a scheme best suitable for nanotube FETs. @FootnoteText@ @footnote 1@S.J. Tans, R.M. Verschueren & C. Dekker, Nature, 393, 49 (1998); R. Martel, T. Schmidt, H.R. Shea, T. Hertel, Ph. Avouris, Appl. Phys. Lett. 73, 2447 (1998).

9:40am **NT+NS+EM+MS-ThM5 Novel Length Scales in Nanotube Devices*, F. Léonard,*** *J. Tersoff,* IBM T.J. Watson Research Center

We calculate the properties of p-n junctions, n-i junctions, and Schottky barriers made on a single-wall carbon nanotube. In contrast to planar bulk junctions, the depletion width for nanotubes varies exponentially with inverse doping. In addition, there is a very long-range (logarithmic) tail in the charge distribution, extending over the entire tube. These effects can render traditional devices unworkable, while opening new possibilities for device design. Our general conclusions should apply to a broad class of nanotube heterojunctions, and to other quasi-one-dimensional ``molecular wire" devices.

10:00am **NT+NS+EM+MS-ThM6 Field Emission from Carbon Nanotubes and Its Application to Electron Sources in Display Elements*, Y. Saito,*** Mie University, Japan*; S. Uemura,* Ise Electronics Corp., Japan **INVITED**

Carbon nanotubes posses the following properties favorable for field emitters: (1) high aspect ratio, (2) small radius of curvature at their tips , (3) high chemical stability and (4) high mechanical strength. Field emission microscopy was carried out for both multiwall nanotubes (MWNTs) and single-wall nanotubes (SWNTs) produced by arc discharge between carbon. Four kinds of nanotubes were investigated; viz., (1) as-grown MWNTs prepared in the helium arc (called "pristine MWNTs"), (2) as-grown MWNTs in hydrogen ("nanog rafibers"), (3) purified MWNTs with open ends ("purified MWNTs" or "open MWN Ts"), and (4) purified SWNTs. Field emission patterns as well as current versus voltage characteristics and Fowler-Nordheim plots for respective nanotubes will be discussed. As an application of nanotube field emitters, we manufactured cathode-ray tube (CRT) type lighting-elements and vacuum-fluorescence display (VFD) panels. In both display elements, conventional thermionic cathodes were replaced with MWNT field emitters which were fixed onto a stainless steel cathode by using conductive paste. In CRT-type lighting elements, the nanotube cold cathode was covered with a grid electrode, the gap between the cathode and the grid being in a range from 0.2 to 0.7 mm. Current density on the cathode surface was on the order of 10 - 100 mA/cm@super 2@ at an average field strength of 1.5 V/ µm. Luminance of the phosphor was intense enough for practical use; e.g., 6.3x10@super 4@ cd/m@super 2@ for green light at an anode current of 0.2 mA and an anode voltage of 10 kV. A direct-current driving test revealed a lifetime over 10,000 hours.

10:40am **NT+NS+EM+MS-ThM8 Emission Properties of Large-area, Fully-sealed Carbon Nanotube Field Emission Display*, W.B. Choi,*** *H.Y. Kim, D.S. Chung, J.H. Kang, I.T. Han, J.M. Kim,* Samsung Advanced Institute of Technology, Korea

Fully sealed field emission display (FED) in size of 4.5 inch has been fabricated by using carbon nanotubes. Carbon nanotubes were fabricated by arc discharge technique. Carbon nanotube aligning techniques with the aid of slurry squeezing and electrophoresis were used for making large-area cathode. The Y@sub 2@O@sub 2@S:Eu, ZnS:Cu,Al, and ZnS:Ag,Cl, phosphors are deposited on the anode glass for red, green, and blue colors, respectively. The assembled structure was sealed in an atmosphere of highly purified Ar gas by means of a glass frit. The display plate was evacuated down to the pressure level of 1x10@super -7@ Torr. Three non-evaporable getters of Ti-Zr-V-Fe were activated during the final heat-exhausting procedure. Finally, the active area of 4.5-inch panel with fully sealed carbon nanotubes was produced. The turn-on field for lighting phosphor was 1.5 V/µm. Brightness of over 1000 cd/m@super 2@ at 4V/µm was achieved on the entire area of 4.5-inch panel from the green phosphor-ITO glass. The fluctuation of the current was satisfied for the field emission display. These reliable results enable us to produce carbon nanotube-based large area full-color FEDs in the near future. In this presentation, fabrication techniques and emission properties of large area carbon nanotube FED will be demonstrated.

11:00am **NT+NS+EM+MS-ThM9 The Structure of Nanotubes Observed with Thermal Field Emission*, K.A. Dean,*** *B.R. Chalamala,* Motorola Flat Panel Display Division*; O. Groening, O.M. Kuettel,* University of Fribourg, Switzerland

We studied the structure of single-walled nanotubes (SWNTs) using field emission microscopy. The field emission images obtained after thermal cleaning depict the spatially-resolved electronic structure of the individual SWNT caps. Using high temperature field emission, we demonstrate how to distinguish between the patterns of individual SWNTs and those of clusters, how to alter the structure of the nanotube cap, and how to extract information about the SWNT structure and chirality from the field emission image. In addition, we demonstrate a technique for measuring the SWNT local density of states through thermal field emission energy distribution measurements. With this technique, we observe that nanotubes have discrete electronic states several eV above the Fermi level, and we suggest that these states are responsible for the large variation in emission current vs. temperature behavior observed among nanotubes.

11:20am **NT+NS+EM+MS-ThM10 Fabrication and Field Emission Properties of Adherent Carbon Nanotube Films*, C. Bower,*** University of North Carolina at Chapel Hill*; W. Zhu, G. Kochanski, S. Jin,* Bell Laboratories, Lucent Technologies*; O. Zhou,* University of North Carolina at Chapel Hill

We report on the fabrication and field emission properties of carbon nanotube films. Films of randomly oriented carbon nanotubes were deposited onto substrates using a variety of techniques. The nanotube films exhibited stable field emission current at low turn-on fields (electric field needed to generate 1 nA of current) and threshold fields (electric field needed to generate 10 mA/cm@super 2@). A single-walled carbon nanotube film with approximately 20% surface coverage showed a turn-on field of 1-1.2 V/µm and a threshold field of 1.3-1.7 V/µm. The emission characteristics deviated from typical Fowler-Nordheim behavior at high current densities. The nanotube films were capable of generating large current densities (> 4 A/cm@super 2@). The emission properties were found to be stable over several days of emitting at 10 mA/cm@super 2@. The emission site density of the films was measured to be 10@super 4@-10@super 5@ sites/cm@super 2@ and the emission patterns were studied.

11:40am **NT+NS+EM+MS-ThM11 Characterization of Oriented Carbon Nanotube Cathodes for Field Emission Flat Panel Display and Light Source Applications*, N.N. Chubun,*** SRPC Istok, Friazino, Russia*; A.G. Chakhovskoi, C.E. Hunt,* University of California, Davis*; A.N. Obraztsov,* Moscow State University, Russia

Oriented carbon nanotubes were recently reported as a viable material for fabrication of field emission cathodes applicable to flat panel displays and vacuum light sources.@footnote 1@ Field emission properties of diode and triode structures with oriented nanotube cathodes were studied in DC-mode in ultra-high vacuum chamber and in sealed glass prototype devices. Cathodes of 9x9mm grown using glow-activated direct current discharge

CVD method on molybdenum and single crystal silicon substrates were studied at currents up to 2 milliamps using metal or phosphor coated anodes. The nanotubes exhibited various degrees of initial surface orientation depending on parameters of the deposition process. An additional orientation of the nanotubes in electric filed during first activation of the cathodes was observed. Monochrome low-voltage FPD phosphors were used for cathodoluminescent brightness/light efficiency characterization and for monitoring of distribution of the filed emission sites. Turn-on voltages varied from 1 to 5 V per micron depending on the extraction electrode configuration. Influence of vacuum conditions and initial training on stability and lifetime of the cathodes was studied. I/V characteristics of the nanotube cathodes were directly compared to those of carbon fiber and carbon foam emitters and to diamond-coated field emission arrays showing potentially greater reproducibility and uniformity of filed emission of the oriented nanotube cathodes. @FootnoteText@ @footnote 1@ A.N.Obraztsov, I.Yu.Pavlovsky, A.P.Volkov, V.L.Kuztetsov, A.L.Chuvilin. MRS 1999 Spring Meeting, San Francisco, CA, April 1999, p.B.4.9/C.2.9.

Plasma Science and Technology Division
Room 609 - Session PS-ThM

Plasma-Surface Interactions II

Moderator: S. Han, UC Berkeley

8:20am **PS-ThM1 Theoretical Analysis of the Interactions of Chemically Reactive Clusters from Silane Plasmas with Crystalline and Amorphous Silicon Surfaces***, **S. Ramalingam**[1], E.S. Aydil, D. Maroudas,* University of California, Santa Barbara*; W.M.M. Kessels,* Eindhoven University of Technology, The Netherlands

Silane containing discharges are used commonly for depositing hydrogenated amorphous silicon (a-Si:H). The structure and electronic properties of the film are determined by the identities and fluxes of the species that impinge and react on the deposition surface. In this presentation, we focus on the interactions with Si surfaces of bare and hydrogenated Si clusters, which can be present in significant concentrations in the plasma. We have conducted a systematic analysis, through classical molecular dynamics (MD) simulations, to study the interactions of Si@sub n@H@sub y@ clusters originating in a SiH@sub 4@ discharge with pristine and H-terminated crystalline Si (c-Si) surfaces and a-Si:H deposited on c-Si. The investigated parameters include the molecular orientation of the cluster, the impingement location on the surface, the kinetic energy of the impinging cluster, and the substrate temperature. The structures and energetics of the Si@sub n@H@sub y@ clusters predicted by the empirical interatomic potential are in good agreement with ab initio results available in the literature. The MD simulations show that the clusters react with unit probability on the pristine Si(001)-(2X1) surface and with nearly unit probability on the H-terminated Si(001)-(2X1) surface. The clusters distort considerably upon attachment to the surface. For example, the Si@sub 6@H@sub 13@ cluster contains a two-fold coordinated H atom, which frequently loses one of its bonds with a Si atom upon reaction with the surface. This leads to the formation of brush-like configurations on the surface of the film, which often collapse on the surface to form more compact structures. The high reactivity of these clusters with Si surfaces and their distortion upon reaction with the surface are explained by the strained nature of the bonds in the original gas-phase clusters. The Si atoms of the cluster often attach preferentially at the center of the dimer bond, and either weaken or break this bond.

8:40am **PS-ThM2 Hydrogen Atom Reactions in a-SiC:H Film Growth***, M.-S. Lee, **S.F. Bent**,* Stanford University

The reactive hydrogen flux in plasma-enhanced chemical vapor deposition has an influential role on film growth both by acting as an excitation source and by altering growth pathways. In this work, the role of hydrogen and the evolution of hydride groups during growth and post-growth treatment of hydrogenated amorphous silicon carbon alloys (a-SiC:H) is investigated. Because the film properties depend on the hydrogen distribution in the films, understanding the hydrogen reaction pathways is important for developing control over the material properties. Thin a-SiC:H films were grown by several methods, including plasma-enhanced chemical vapor deposition (CVD) and hot-wire CVD. Methylsilanes were used as single source precursors in a low pressure regime between 200 and 600 K. In situ vibrational spectroscopy was used to provide a detailed identification of the hydride bonding in the film, and near-edge X-ray absorption fine structure (NEXAFS) provided supporting information on carbon and silicon bonding. Studies were made of the effect of H@sub 2@ dilution and post-growth hydrogenation, using isotopic labelling. These experiments were complemented by temporal studies of deuterium exchange reactions, which were used to monitor and differentiate the elementary reactions between D atoms and SiH@sub x@ and CH@sub x@ groups in the material. Different kinetic rates and temperature dependences were observed for the reaction of D with silicon- vs carbon-hydride groups. For the SiH@sub x@ groups, rapid exchange was followed by a slower insertion mechanism; the less facile CH@sub x@ loss was not followed by a detectable increase in CD@sub x@, suggesting that etching or C=C formation may be more important for carbon. These reactions, and their temperature dependence, have important consequences for the final film structure and properties.

9:00am **PS-ThM3 An In Situ Study of Plasma Deposition of Hydrogenated Amorphous Silicon Using Multiple Total Internal Reflection Infrared Spectroscopy***, **D.C. Marra**,* University of California, Santa Barbara*; W.M.M. Kessels,* Eindhoven University of Technology, The Netherlands*; B.F. Hanyaloglu, E.S. Aydil,* University of California, Santa Barbara

Multiple total internal reflection Fourier transform infrared spectroscopy (MTIR-FTIR) was used to study plasma enhanced chemical vapor deposition of hydrogenated amorphous silicon in situ and in real time. Several methods using MTIR infrared spectroscopy are combined to study the hydrogen bonding on a-Si:H surfaces as well as the spatial distributions of hydrides in the bulk film. A new technique for identifying surface adsorbates on plasma deposited films combines the sensitivity of in situ attenuated total reflection FTIR with Ar ion assisted desorption of surface species. The dependence of the silicon hydride coverage on the substrate temperature between 40 and 370@degree@C as a function of discharge power and pressure is investigated. As expected, fewer higher hydrides exist on the surface at elevated deposition temperatures. However, this observation is not universal and depends strongly on the discharge pressure and the power. In fact, the temperature dependence of the surface hydrides is less critical to the coverage than the ion bombardment. A careful study of the effect of Ar ion bombardment on a-Si:H surfaces and near surfaces has enabled experimental observation of isolated H at Si-Si bond center sites. Hydrogens at bond center sites appear to be created during deposition and are metastable. During the first 30 minutes after deposition, Si-H-Si bonds are broken and at least some of these H form more stable SiH, SiH@sub 2@and SiH@sub 3@ bonds either in the film and/or on the surface. Hydrogen concentration distribution and bonding as a function of depth in plasma deposited a-Si:H films were also studied using MTIR-FTIR in conjunction with in situ spectroscopic ellipsometry. Immediately below a hydrogen rich surface layer there is a few hundred Angstrom thick subsurface region that is depleted in H compared to the bulk film. Ion bombardment is shown to be responsible for this hydrogen-depleted layer.

9:20am **PS-ThM4 Plasma and Surface Chemistry in a Remote Silane Plasma Studied By Various Diagnostics and Related to a-Si:H Film Quality***, **W.M.M. Kessels**[2], M.C.M. van de Sanden, A.H.M. Smets, B.A. Korevaar, D.C. Schram,* Eindhoven University of Technology, The Netherlands

A remote silane plasma used for fast deposition of device quality a-Si:H has been studied in detail and information about the contribution of particular species to film growth has been obtained. The creation and fluxes of silane radicals have been studied by means of various diagnostics like appearance potential mass spectrometry (SiH@sub 3@, SiH@sub 2@,H), UV absorption spectroscopy (SiH@sub 3@) and optical emission spectroscopy (SiH, Si). From ion mass spectrometry, revealing hydrogen poor cationic clusters up to Si@sub 10@H@sub n@@super +@, in combination with Langmuir probe measurements, the downstream ion chemistry is studied. It is shown that the deposition is dominated by radicals, while the ions have a contribution of approximately 7% to film growth. The silane radicals created can be influenced by changing the plasma source operation. It is shown that the deposition of a-Si:H can be altered from a SiH@sub 3@ dominated growth to a situation in which reactive silane radicals contribute significantly. This is accomponied by a decrease of the compound value for the surface reaction probability, as determined by an aperture-well assembly, a decrease of the film surface roughness and an improvement of the film quality in terms of structural and opto-electronic film properties. The compound value of the surface reaction probability is 0.33±0.05 for the

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

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

conditions in which device quality a-Si:H is obtained. The role of the specific species in film growth and their influence on film properties is discussed.

9:40am **PS-ThM5 Competition Between Etching and Deposition in Methane/Hydrogen Plasma Interactions with the Si(100) Surface***, **H.L. Duan**, S.F. Bent,* Stanford University

The addition of hydrogen to alkane-based plasmas is important in a number of applications, including diamond synthesis and compound semiconductor etching. However, the mechanisms by which hydrogen influences the plasma system are not fully understood. In this study, optical and mass spectroscopic methods have been carried out to acquire a molecular level understanding of methane/hydrogen plasma interactions with a Si (100) surface. The plasma was formed via an electron cyclotron resonance (ECR) plasma source. Multiple internal reflection Fourier transform infrared (MIR-FTIR) spectroscopy and real time in situ mass spectrometry were used to probe the time evolution of surface and gas species at the plasma surface interface. The results show that in the absence of added hydrogen, a polymer-like a-C:H film is deposited on the silicon surface with a linear growth rate. Addition of hydrogen into the plasma, depending on the methane-to-hydrogen ratio, can lead to a complete suppression of film growth; the steady-state coverage of hydrocarbon is about ten monolayers according to the FTIR results. At the same time, infrared absorption at the SiH stretching frequencies suggests a comparable coverage of silicon hydrides. These results together indicate that significant roughening of the silicon surface occurs, and suggest the possibility of etching. This conclusion is supported by preliminary mass spectrometric results indicating the presence of etch products during reaction. For the same plasma conditions, increasing the surface temperature increases the initial a-C:H film growth rate. However, even at elevated temperatures, growth can be suppressed by the addition of hydrogen. The experimental results indicate that there is a competition between etching and deposition chemistry determined by the methane-to-hydrogen ratio in the plasma. Proposed mechanisms describing this competition, and the possibility of etching of silicon by methyl species, will be discussed.

10:00am **PS-ThM6 A Multi-dimensional Model for an Inductively Coupled Ar/C@sub 4@F@sub 8@ Discharge***, **S. Rauf**, P.L.G. Ventzek, V. Arunachalam, D.G. Coronell,* Motorola Inc.

Plasmas based on complex fluorocarbons such as C@sub 4@F@sub 8@ are the main workhorse for SiO@sub 2@ etching in the microelectronics manufacturing industry. To understand the etching mechanism and how important process parameters (e.g. etch rate, uniformity) are related to typical actuators (e.g. gas pressure, power), we have recently developed a 2-dimensional model for an inductively coupled Ar/C@sub 4@F@sub 8@ discharge. The model is based on the Hybrid Plasma Equipment Model, a comprehensive plasma equipment simulation tool developed at the University of Illinois. For this project, the plasma is treated as a fluid and rates for various electron impact processes are computed using a homogeneous Boltzmann equation solver. The gas phase chemical mechanism includes electron impact ionization, dissociation and attachment processes for C@sub 4@F@sub 8@ and its C@sub x@F@sub y@ progeny, ion-ion and ion-molecule chemistry. A reasonably detailed description of surface processes at the SiO@sub 2@ coated wafer is also included. The plasma reactor model is coupled to an external circuit model. The model was used to simulate Ar/C@sub 4@F@sub 8@ based plasmas in the inductively coupled Gaseous Electronics Conference reference cell. C@sub 4@F@sub 8@ concentrations were between 10-50%, gas pressure was varied between 10-30 mTorr and total inductive power deposition was 300-700 W. Results show that most of the incoming C@sub 4@F@sub 8@ dissociates quite rapidly near the inlet into CF@sub x@ (x = 1,2,3) radicals. Substantial amount of C@sub 2@F@sub 4@ is also present in the discharge. The plasma is moderately electronegative with F@super -@ being the major negative ion. Implications of control parameters on the plasma characteristics and etching kinetics will be discussed.

10:20am **PS-ThM7 Inorganic Plasma Low-k Materials - Aurora 2.7 -***, **N. Matsuki**, Y. Morisada, Y. Naito, A. Matsunoshita,* ASM Japan K.K., Japan

Methyl-SiO and Phenyl Methyl-SiO interlayer dielectric (ILD) films with dielectric constants in the 2.6 to 3.0 range were successfully obtained by PE-CVD method. Precursors used to deposit these low-k films were Dimethyldimethoxysilane Si (CH@sub 3@)@sub 2@(OCH@sub 3@)@sub 2@ and Phenylmethyldimethoxysilane Si (C@sub 6@H@sub 5@) (CH@sub 3@)(OCH@sub 3@)@sub 2@, respectively. Reaction gases consisting one of these precursors and some additive gas such as He or H@sub 2@ were introduced into the Eagle-10 reaction chamber with conventional parallel plate electrodes. These films were deposited in 400 @super o@C plasma process without an anneal step. Residence time of gas molecules in the reaction space was prolonged to enhance disintegration and polymerization in the gas phase. FT-IR data suggest that these plasma low-k films have stable Si-O network structure incorporating hydrocarbons (-CH3 or -C6H5), thus avoiding Si-OH formation. TDS and TGA data show these films have high thermal stability up to 500 @super o@C. The dielectric constant did not increase after a pressure cooker test at 120 @super o@C and RH 100% for an hour. The leakage current was found to be 10@super -9@ (A/cm@super 2@) at 2 MV/cm. The surface roughness was less than 5 nm (1µm film, P-V). The CMP rate was less than 5 nm/min using Cu CMP slurry at a Cu polishing speed of 300 nm/min. Thus, it appears that these stable low-k films have ideal properties for Cu damascene metallization insulation layers.

10:40am **PS-ThM8 Plasma Modification of Polymeric Membranes***, **M.L. Steen**, E.R. Fisher, N.E. Capps, E.D. Havey,* Colorado State University

Since most polymers have intrinsically low surface energy, poor adhesion and wettability severely limit many applications. The adhesion properties and wettability of polymers can be improved through plasma surface modification. The surface properties altered by plasma treatment include chemical composition, wettability and adhesion. These properties depend on the interaction of the plasma with the surface. Specifically, the plasma can often erode the polymer, abstracting atoms and breaking polymer chains. Reactive species in the plasma can interact at these active sites, thereby, implanting new functional groups. Alternatively, the plasma can also change the surface properties of the polymer by depositing a thin, conformal film on the surface. The primary goal of our research is to develop plasma-based treatments that render the surface of hydrophobic polymeric membranes permanently hydrophilic. A related goal is to investigate plasma treatments that produce highly hydrophobic materials. We have done an extensive parameter study of many plasma systems. For the hydrophilic treatments, we have studied OH implantation from pure H@sub 2@O plasmas and H@sub 2@O plasmas with a diluent gas, such as Ar. For the hydrophobic treatments, we have studied F atom implantation from CF@sub 4@ plasma. The membrane can also be rendered hydrophobic by depositing a fluorocarbon film from a pulsed CHF@sub 3@ plasma. We have also combined these two approaches by first depositing a hydrocarbon film from CH@sub 4@ and then fluorinating that film with a reactive gas, such as CF@sub 4@. Results from bubble point measurements, porometry, SEM, contact-angle measurements and gas permeability identify several plasma treatments that successfully impart these membranes with the desired surface properties. Specifically, Ar/H@sub 2@O, CF@sub 4@, CHF@sub 3@ and CH@sub 4@/CF@sub 4@ plasma treatments will be discussed.

11:00am **PS-ThM9 Polymer Surfaces Modified Using RF Plasma***, **D.A. Steele**, R.D. Short,* University of Sheffield, UK*; D. Barton, J.W. Bradley,* UMIST, UK

The properties of a cold plasma are investigated using Langmuir probes and the resultant surface treatments of polystyrene studied using XPS. A glass walled reactor vessel, powered with a matched RF (13.56 MHz) supply via external excitation coil, is utilized to study the capacitively coupled plasma of argon gas. Plasma and self-bias potentials, densities and electron temperatures are investigated using compensated Langmuir probes over a range of input powers and gas pressures. At a 10W nominal input power and gas pressure of 10 mTorr the plasma has a density of 3 x 10@super 15@ m@super -3@ and an electron temperature of 2.5 eV, with an ion mean energy of almost 30 eV. Under such conditions we rationalize that, in the outermost 20Å of a polystyrene substrate, the energy deposited by ions (2.8 mW cm@super -2@) is an order of magnitude greater than that from the VUV photons. However assumptions of a model system, with a pure argon gas plasma and a polystyrene substrate free from UV absorbing impurities, have been made where the effects of residual air and desorption of water from the reactor walls are neglected. Further studies continue to determine the magnitude of these assumptions on polymer modification so a more accurate model of ion/photon energy deposition can be made.

Surface Science Division
Room 606 - Session SS1+AS+BI-ThM

Self-Assembled Monolayers

Moderator: N.D. Shinn, Sandia National Laboratories

8:20am **SS1+AS+BI-ThM1 Two-Dimensional Phase Transitions in Amphiphile Monolayers***, **G.E. Poirier**,* National Institute of Standards and Technology

Recently scientists have explored methods of constructing complex chemically patterned surfaces with the goal of making novel biosensors or of realizing lab-on-a-chip technology. In order to design patterned monolayers it is important to understand how these molecules behave in two dimensions, what is the molecular packing of the surface phases and which phases coexist in thermodynamic equilibrium. The goal of this presentation is to describe the two-dimensional structural phases of decanethiol monolayers. Our studies were conducted using gas-phase transport of decanethiol onto clean Au(111) in an ultrahigh vacuum scanning tunneling microscope. With increasing surface coverage, the monolayer sequentially adopts six discrete structural phases. At low surface coverage, decanethiol exists as a lattice 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, but with discretely increasing degrees of out-of-plane interdigitation. Above saturation coverage of the densest surface-aligned phase, the monolayer undergoes an edge-mediated melting transition. The c(3x2/3) phase, characterized by alignment of the molecular axes close to the surface normal, nucleates and grows from this liquid. These studies provided a detailed, real-space picture of the coverage-dependent phases and phase transitions of alkanethiol molecular monolayers on Au(111).

8:40am **SS1+AS+BI-ThM2 Surface Phase Transitions of Asymmetric Dialkyl Disulfide Self-Assembled Monolayers***, **M. Hara**, K. Kamei, T. Araki, K. Fujita, W. Knoll,* Frontier Research Program, RIKEN, Japan

Adsorption and desorption processes of asymmetric dialkyl disulfide (hexyl octadecyl disulfide: C6-SS-C18) self-assembled monolayers (SAMs) on Au(111) have been investigated by surface plasmon resonance (SPR), mass spectroscopy (MS), thermal desorption spectroscopy (TDS), and scanning tunneling microscopy (STM). Formation of C6-SS-C6 and C18-SS-C18 dimer species in the monolayer and also in the solution through dimerization and exchange processes has been confirmed during the monolayer growth. In the TDS spectra for shorter immersion SAMs, C6 monomer species showed the strong peaks, and gradually C6-SS-C6 dimer and C18 monomer peaks become stronger for longer immersion. Phase-separated domains of pure C6 and pure C18 striped phases have been visualized in the initial growth stage by STM and the area of the C6 domain was larger than that of C18 one. These results suggest that S-S bonds were cleaved when disulfides adsorbed on Au surface followed by the surface diffusion to form phase separation before standing-up SAM formation. After the C6-rich SAM growth, molecules are dimerized and then exchange process starts from the weakly bound C6-SS-C6 dimers toward C18-rich SAM. SPR kinetics studies also showed the double exponential growth which is different from usual Langmuir adsorption isotherm. Following those results, we propose more detailed surface phase transition model of alkanethiol SAM growth through the dimerization and the exchange processes.

9:00am **SS1+AS+BI-ThM3 Structure, Bonding and Reactivity of Self-assembled Monolayers***, **G.J. Leggett**, B.D. Beake, N.D. Brewer,* UMIST, UK*; E. Cooper,* Glaxo-Wellcome, UK*; D.A. Hutt,* University of Loughborough, UK

Two approaches to the characterisation of the nature of the sulfur bonding environment in self-assembled monolayers (SAMs) have been explored: sulfur K-edge surface extended X-ray absorption fine structure (SEXAFS) and static secondary ion mass spectrometry (SIMS). S K-edge SEXAFS has proved highly effective for SAMs on Ag and has confirmed that the sulfur adsorbs with threefold coordination during both solution-phase adsorption onto polycrystalline Ag and gas-phase adsorption onto Ag(111) single crystal surfaces. There is no change in the S adsorption site with coverage. Static SIMS has yielded powerful insights into the effect of electron beam bombardment on SAM structure. A complete loss of all gold-molecular fragments from the spectrum is observed after small doses of electrons, indicating a rapid alteration of the sulfur bonding environment, due either to S-C bond scission or, more likely, to oxidation of thiolates to disulfides. Changes in Au-S bonding during the formation of the low coverage phase of butanethiol on Au have also been studied by static SIMS. Photo- and air-oxidation rates are influenced by the adsorbate alkyl chain length; rates of both processes decrease with increasing chain length due to increasing SAM ordering. The nature of the terminal group also affects rates of oxidation, and has a profound influence on the stability of the SAM. Hydrogen bonding between neighbouring terminal groups leads to significant stabilisation. Friction coefficients may be measured for SAMs using friction force microscopy. These decrease with increasing alkyl chain length, and are higher for adsorbates with polar terminal groups. Oxidation of methyl terminated SAMs leads to an increase in the coefficient of friction, interpreted in terms of the collapse of film order following head group oxidation. The rate of increase in the coefficient of friction is faster for short chain SAMs than long-chain SAMs, in agreement with the findings of static SIMS studies.

9:20am **SS1+AS+BI-ThM4 Structure of Partially Fluorinated n-alkanethiols on Polycrystalline Gold and Silver Surfaces***, **S. Frey**,* Universität Heidelberg, Germany*; K. Tamada,* National Institute of Materials and Chemical Research, Japan*; K. Heister, M. Zharnikov, M. Grunze,* Universität Heidelberg, Germany

The physical and chemical properties of self-assembled monolayers (SAM) of alkanethiols (AT) are noticeably affected by partial fluorination of the hydrocarbon chain. We have studied the structure of SAMs formed from partially fluorinated alkanethiols (PFAT) CF@sub 3@(CF@sub 2@)@sub 9@(CH@sub 2@)@sub n@SH with different hydrocarbon chain length (n = 2, 11 and 17) on Au and Ag coated silicon wafers. The objectives of our experiments were (i) to find out whether PFAT form ordered and densely packed SAMs on these substrates, (ii) to determine the individual conformation and orientation of the hydro- and fluorocarbon parts in the molecules, and (iii) to clarify the influence of the headgroup-metal bond (RS-Au or RS-Ag) on the film structure. The PFAT films were characterized by atomic force microscopy, infrared reflection absorption spectroscopy, X-ray photoelectron spectroscopy, and angle resolved near edge X-ray absorption fine structure spectroscopy. PFATs were found to form highly ordered and densely packed SAMs on polycrystalline Au and Ag. The hydrocarbon and fluorocarbon chains of the adsorbed PFATs retain the expected planar zigzag and helical conformation of the bulk materials, respectively. The fluorocarbon chains, which are oriented almost perpendicular to the substrates for CF@sub 3@(CF@sub 2@)@sub 9@(CH@sub 2@)@sub 2@SH, assume a more tilted orientation in PFAT SAMs with longer hydrocarbon moieties. As found for the AT on Ag and Au, the hydrocarbon part in the PFAT films exhibits smaller tilt and twist angles on Ag as compared to the Au substrates. Considering the reduced van der Waals interaction between the hydrocarbon chains in PFAT as compared to neat AT SAMs (due to the sterical constraints provided by the fluorocarbon chains), the differences in tilt and twist angle appears to be associated with the different character of the headgroup-substrate bonding on Au and Ag. This work has been supported by the German Bundesministerium für Bildung, Wissenschaft, Forschung und Technologie through grant No. 05 SF8VHA 1.

9:40am **SS1+AS+BI-ThM5 Controlling the Placement of Molecules in the Self Assembly and Directed Assembly of Organic Monolayers***, **P.S. Weiss**, D.L. Allara, L.A. Bumm, J.J. Jackiw,* The Pennsylvania State University **INVITED**

We manipulate and measure the structures of monolayer films in order to tune their properties. This is accomplished by controlling the defect type and density in the films. We then process the films to insert single molecules, to insert bundles of molecules, or to graft new molecular terraces onto existing domains by using these defects to advantage. The inserted molecules can serve as the anchor points for polymerization; this allows us to choose to produce single polymer dots or isolated polymer brushes. We connect our scanning tunneling microscopy measurements to electron transfer phenomena which are ubiquitous in such areas as biochemistry and electrochemistry by separating the transconductance into components arising from transport through the molecule vs. the tunneling gap outside the film. We show how these components can be measured independently. We prepare films predicted to have many equivalent defect sites so as to provide identical matrix isolation environments for single molecular wire candidates. We also prepare films with well defined interfaces between separated components so that insertion, deposition, or reaction can be directed to these molecularly sharp boundaries.

10:20am **SS1+AS+BI-ThM7 Protein Adsorption to Model Surfaces: Probe Adhesion Between Fibrinogen and Patterned SAMs**, ***L.F. Pardo***, *T.B. Boland,* Clemson University

Interactions between blood and an artificial surface induce a rapid, thrombogenic response believed to be mediated by protein adsorption. In this study, atomic force microscopy (AFM) was used to measure directly non-specific forces between proteins and functionalized surfaces. A protein-modified AFM cantilever tip was used to probe of interactions between a model substrate and a single protein. Model surfaces consisted of both simple and microcontact-printed, -OH, -COOH, and -CH3 terminated self-assembled monolayers (SAMs) of alkanethiols on gold. Fibrinogen was used as the model protein due to its significance in biomaterial-mediated inflammatory responses. It was tethered to the probe tip using a synthetic polypeptide (polyserine). Various approaches were taken to link polyserine to a self-assembled monolayer on a gold substrate. Ellipsometric and vibrational spectroscopic measurements indicated that successive carbodiimide activation of a carboxyl-terminated alkanethiol and polyserine allowed for the successful formation of a polyserine-tethered fibrinogen film. The SAMs, polyserine and fibrinogen films were characterized by ellipsometry and contact angle measurements. Both AFM images and measurements will be presented and discussed. An understanding of how fibrinogen interacts under model conditions will give insight into more complicated real systems.

10:40am **SS1+AS+BI-ThM8 Modification of Self-Assembled Monolayers by X-ray, Electron and Thermal Treatments**, ***H. Fairbrother***, *A. Wagner, K. Han,* Johns Hopkins University

Polymer surface modification strategies are widely used to modify interfacial characteristics, including permeability, wettability, adhesion, friction, wear and biocompatibilty. To better understand the detailed nature of these processes thiol-based self-assembled monolayers (SAMs) adsorbed on Au substrates have been used as models for the polymeric interface. In the case of X-ray modification results from X-ray Photoelectron Spectroscopy on fluorinated SAMs show that the degree of cross-linking can be directly correlated with the appearance of CF groups in the organic film. Additional information from Reflection Absorption Spectroscopy and Atomic Force Microscopy on the impact of X-ray, electron, and thermal modification treatments will also be presented, enabling a detailed picture of the chemical and physical modifications that occur during surface treatments to be constructed.

11:00am **SS1+AS+BI-ThM9 Electron-induced Damage in Thio-functionalized Alkanethiol Monolayers**, ***K. Heister***, *W. Geyer, S. Frey,* Universität Heidelberg, Germany; *A. Ulman,* Polytechnic University; *A. Gölzhäuser, M. Zharnikov,* Universität Heidelberg, Germany

Potential technological applications of self-assembled monolayers (SAM) of alkanethiols (AT) as lithographic resist require an increased sensitivity of these systems toward ions, X-ray photon or electron irradiation. This effect can be achieved by incorporation of specific molecular groups associated with comparatively weak bonds, such as C-S bond provided by sulfide -S- and sulfone SO@sub 2@- moieties, in the aliphatic chains. We have investigated the damage induced by low-energy electrons in SAMs formed from C@sub 6@H@sub 13@SC@sub 11@H@sub 22@SH (I), C@sub 6@H@sub 13@SO@sub 2@C@sub 11@H@sub 22@SH (II), C@sub 11@H@sub 23@SO@sub 2@C@sub 6@H@sub 12@SH (III), and C@sub 11@H@sub 23@SO@sub 2@C@sub 6@H@sub 4@OC@sub 5@H@sub 10@SH (IV) on polycrystalline Au substrates using angle-resolved near edge X-ray absorption fine structure spectroscopy and X-ray photoelectron spectroscopy. Similar to AT SAMs, an irradiation-induced disordering and a dehydrogenation of the pristine films I - IV as well as the desorption of molecule fragments and the transformation of thiolate moieties in a new irradiation-induced sulfur species were observed. The extent of the irradiation-induced events is, however, affected by the introduction of the sulfide and sulfone moieties. An increased extent of the irradiation-induced desorption processes as compared to AT SAMs was found in I and II, which implies that bond scission events predominately occur in the outermost part of AT SAM. Controversially, an additional dipolar interchain interaction provided by the sulfonic entities has a stabilizing influence on the lower part of SAMs II-IV leading to the conservation of the pristine thiolate species responsible for anchoring of the alkyl chains to the substrate. Considering these controversial effects provided by the sulfonic groups the incorporation of sulfide moiety seems to be a better choice to improve the sensitivity of AT SAMs toward electron irradiation.

11:20am **SS1+AS+BI-ThM10 Sensitivity of Alkanethiol Self-assembled Monolayers toward Low-energy Electron Irradiation**, ***M. Zharnikov***, *S. Frey, K. Heister, M. Grunze,* Universität Heidelberg, Germany

Potential technological applications of self-assembled monolayers (SAM) as lithographic resist involve their exposure to ions, X-ray photons or electrons. We have investigated the damage induced by low-energy electrons in SAMs of dodecanethiolate (DDT), octadecanethiolate (ODT) and perdeuterated eicosanethiolate (PDET) on gold and of ODT on silver using x-ray photoelectron spectroscopy and angle resolved near edge x-ray absorption fine structure spectroscopy. ODT/Au was taken as a reference system, whereas the other SAMs differed from ODT/Au in the length (DDT/Au) and the isotopic composition (PDET/Au) of the alkyl chains and the strength and character of the thiolate-metal bond (ODT/Ag). All systems studied were found to exhibit a qualitatively similar behavior with respect to low-energy electron irradiation. Both the alkyl chains and the S-Au interface are affected simultaneously through the electron-induced dissociation of C-H, C-C, C-S, and metal-thiolate bonds. The most noticeable processes are the loss of the orientational and conformational order, partial dehydrogenation with C=C double bond formation, desorption of film fragments, decrease of thiolate species, and the appearance of new sulfur species. The cross sections for the individual irradiation-induced processes have been determined. The reactions of the alkyl matrix and the S-metal interface to electron irradiation are essentially independent. The extent and rate of thiolate species reduction and new sulfur species formation are mainly determined by the strength and character of the thiolate-metal bond (Au vs. Ag). At the same time, an extent of irradiation-induced desorption of sulfur-containing fragments depends on the alkyl chain length. Only a slight isotopic variation in the irradiation-induced dehydrogenated process was observed.

Surface Science Division
Room 607 - Session SS2+EM+NS-ThM
Nucleation and Growth

Moderator: G.M. Nathanson, University of Wisconsin, Madison

8:20am **SS2+EM+NS-ThM1 Evolving Surface Morphology: An In Situ STM Study of 2-20 nm SiGe Quantum Wells Grown on 75 mm Si (100) Wafers**, ***G.G. Jernigan***, Naval Research Laboratory, US; *P.E. Thompson,* Naval Research Laboratory

Electrical device improvement will come from the understanding and control of interfaces at the atomic level. We have integrated an STM with a commercial Si MBE system for in situ examination of device structures grown on full 75 mm wafers. Our first system of study is the growth of SiGe quantum wells on Si (100). SiGe is being investigated for its use in optoelectronics and high speed circuits. We will present a description of the atomic surface morphology of the initial 100 nm epitaxial Si buffer layer, followed by a Si@sub 0.8@Ge@sub 0.2@ quantum well of thickness up to 20 nm, and a Si capping layer deposited after the quantum well. The Si buffer layer is grown using a 0.08 nm/s Si flux onto a 650 @super o@C substrate. Step-flow growth occurs, but the different adatom sticking probabilities at the S@sub A@ and S@sub B@ steps produces a "wavy" surface which is the result of alternating terraces growing rapidly in different directions rotated by 90@super o@. The deposition of Si@sub 0.8@Ge@sub 0.2@, by co-depositing Ge with a 0.02 nm/s flux and Si, disrupts the "wavy" growth morphology. Ge segregation during deposition produces a "2xn" surface reconstruction that consists of rows which run perpendicular (G@sub A@) and parallel (G@sub B@) to a step edge in a manner analogous to the S@sub A@ and S@sub B@ steps, respectively. The quantum well morphology consists of a mosaic of small terraces containing short rows of G@sub A@ steps and long rows of G@sub B@ steps. The Si capping layer grown on the quantum well reinstates the "wavy" morphology. However, in addition to the S@sub A@ and S@sub B@ step-flow growth, dimer vacancy lines are now observed within the S@sub A@ terraces and are due to Ge segregation from the quantum well. The effects of S@sub A@/S@sub B@ waves, Ge "2xn" terraces, and dimer vacancy lines as a function of growth rate and temperature will be discussed. This work was supported by the ONR.

8:40am **SS2+EM+NS-ThM2 Hydrogen-Mediated Surface Morphological Evolution in Si@sub 0.7@Ge@sub 0.3@/Si(001) Layers Grown by Hydride Gas-source Molecular Beam Epitaxy***, **T. Spila**, P. Desjardins, H. Kim, N. Taylor, D.G. Cahill, J.E. Greene,* University of Illinois, Urbana*; S. Guillon, R.A. Masut,* Ecole Polytechnique de Montréal, Canada

The primary mechanisms for relieving misfit strain @epsilon@ during heteroepitaxy are the formation of misfit dislocations (MD) and strain-induced roughening. These mechanisms are initially competing (due to @epsilon@-dependent activation energies) and eventually interacting once relaxation is initiated. Si@sub 0.7@Ge@sub0.3@ layers were grown on Si(001) (miscuts @<=@ 0.1°) to quantitatively investigate the effects of Ge surface segregation and steady-state hydrogen coverage @theta@@sub H@ on mechanisms of surface morphological evolution during GS-MBE from Si@sub 2@H@sub 6@/Ge@sub 2@H@sub 6@. For growth temperatures T@sub s@ > 600 °C where @theta@@sub H@ = 0, layers exhibit (by AFM and XTEM) surface morphologies similar to that observed in solid-source MBE. The islanding process observed at T@sub s@ = 800 °C relieves 45% of the strain (determined from x-ray reciprocal lattice maps) without the introduction of MDs for thicknesses t up to 31 nm. The dominant facet planes evolve from {105}/{113} to {518}/{111}/{011} with increasing t until coalescence (t = 180 nm). Decreasing T@sub s@ < 600 °C to a regime where @theta@@sub H@ > 0 allows an opportunity to probe new hydrogen-mediated surface morphological pathways. The tendency toward strain-induced roughening and faceting decreases with decreasing T@sub s@ as the initial low-thickness strain-relaxation mechanism and corresponding in-plane feature size changes from strain-induced roughening to MD nucleation when T@sub s@ is decreased below 525 °C. We discuss the details of surface morphological evolution in each of the three temperature regimes (< 525, 525-600, and > 600 °C) in terms of local precursor adsorption and H-desorption kinetics.

9:00am **SS2+EM+NS-ThM3 Interdiffusion During Growth of Ge on Si(100)***, **H. Jonsson**, B.P. Uberuaga, M. Leskovar, B.R. Schroeder, S. Meng, M.A. Olmstead,* University of Washington

We present both experimental evidence and a theoretical explanation of sub-monolayer Ge epitaxy on Si(100) interdiffusion to the 4th layer of the Si substrate. XPD measurements at both 500 C and 700 C show the presence of Ge atoms in the 4th layer. DFT/GGA calculations of the energetics of a Ge atom in the Si surface, together with a statistical model of Ge occupation of the lattice sites, predict occupation of sub-surface sites, with enhanced occupation in the sites under tensile strain. The calculations indicate that the formation energy of a Ge interstitial near the surface (about 1 eV higher energy than the adatom) is significantly reduced as compared with an interstitial in bulk Si, thus lowering the energy barrier for the interstitial diffusion mechanism near the surface. This work was supported by the National Science Foundation, the University of Washington Royalty Research Fund and the Japanese New Energy and Technology Development Organization.

9:20am **SS2+EM+NS-ThM4 Confined Intermixing of Ge and Si***, **S.-J. Kahng**,* Seoul National University, Korea*; Y.H. Ha, D.W. Moon,* Korea Research Institute of Standards and Science, Korea*; Y. Kuk,* Seoul National University, Korea

In Ge-Si superlattice system, the efficiencies of a possible optoelectric and fast devices can be improved by optimizing the composition at each layer and the abruptness at the interface. It is well- known that intermixing between Ge and Si atoms mainly occurs during the growth process of Si layers on the previously grown Ge layers. Ge atoms tend to segregate toward the surface since the surface free energy of Ge is lower than that of Si. Howerver, with hydrogen adsorbate, the surface free energy of Ge is lower than that of Si, possibly inducing segregation of Si in the Ge overlayer. In this study, Si surface segregation was studied quantitatively for the Ge overlayers grown on Si(100)-(2 x 1) with channeled medium energy ion scattering spectroscopy. The intermixing between Ge and Si presents only at the initial layer in the presence of hydrogen surfactant. Microscopic mechanism for the growth process will be discussed in the view point of kinetics as well as energetics.

9:40am **SS2+EM+NS-ThM5 Surface Segregation and Surface Reactivity in Heteroepitaxial Vapor Phase Thin Film Growth: Si@sub 1-x@Ge@sub x@ on Si(111)***, **Y.-J. Zheng**, A.M. Lam, J.R. Engstrom,* Cornell University

Supersonic molecular beam scattering, x-ray photoelectron spectroscopy (XPS) and low-energy ion scattering spectrometry (LEISS) have been employed to examine the heteroepitaxial growth of Si@sub 1-x@Ge@sub x@ thin films on Si(111) surfaces. Molecular beam scattering has been employed to measure the reactivity of Si@sub 2@H@sub 6@ and GeH@sub 4@ on the Si@sub 1-x@Ge@sub x@ alloy surfaces for a variety of growth conditions (composition and substrate temperature), and these results are compared with results obtained on the clean Si(111) and Ge(111) surfaces. We find that the alloy surfaces are less reactive than both of the pure elemental Si and Ge surfaces. This is in stark contrast to our results for the (100) orientations, where alloy reactivity was always intermediate to that observed on clean Si and Ge. These results reflect the important role played by surface reconstructions on the (111) orientations. XPS and LEISS have been employed in situ to quantify the near-surface Ge concentration of the Si@sub 1-x@Ge@sub x@ epitaxial thin films. Ge segregation is significant, although somewhat less pronounced compared to what we have observed previously on the (100) orientations. Ge segregation, which occurs also in the subsurface layers, has been successfully modeled using both a statistical thermodynamic analytical model, and Monte Carlo simulations.

10:00am **SS2+EM+NS-ThM6 The Role of Arsenic Surfactant in the Growth of Germanium Thin Films on Si(100) Surfaces***, **C.L. Berrie**, J. Bright, S.R. Leone,* University of Colorado, Boulder

The role of arsenic surfactant in the growth of germanium films on Si(100) substrates is investigated using laser single photon ionization time of flight mass spectrometry, reflection high energy electron diffraction, and atomic force microscopy. The energetics of arsenic interaction with Si(100) and Ge(100) are investigated by monitoring the temperature dependence of the desorbing fluxes of As@sub 4@, As@sub 2@ and As atoms from the substrate under a constant incident As@sub 4@ flux. These measurements indicate that the As@sub 2@ interactions with Si(100) and Ge(100) differ dramatically. In particular, the As@sub 2@ flux plateaus in the case of the Si(100) substrate from 800 K to 1000 K. In the case of the Ge(100) substrate, the As@sub 2@ flux monotonically increases over this temperature range and a similar plateau is not observed. Measurements of the desorbing As@sub n@ fluxes are also made during Ge growth on a Si(100) surface. The dramatic difference in the arsenic interaction on these two surfaces is evident in these measurements as well. The morphologies of the resulting films are monitored ex-situ using atomic force microscopy to determine the effect of arsenic coverage on the size and density distributions of islands formed. As the arsenic coverage is increases, the observed island size decreases and the density of islands increases dramatically. The mechanisms for the Ge growth and the interaction in the presence of the arsenic surfactant will be considered.

10:20am **SS2+EM+NS-ThM7 The Dynamics of the Si(111) (7x7) to (1x1) Phase Transition Investigated by Low Energy Electron Microscopy***, **J.B. Hannon**,* Carnegie Mellon University **INVITED**

We have used low-energy electron microscopy (LEEM) to investigate the dynamics of the (7x7) to (1x1) phase transition on the Si(111) surface. Because the density of the (1x1) surface is 6 percent larger than that of the (7x7) surface, the conversion from (7x7) to (1x1) requires transport of mass to the domain boundary. By measuring the time evolution of complicated configurations of triangular (7x7) domains, and comparing the results to detailed simulations, we are able to quantify the role of mass transport in the dynamics of this phase transition. We find that individual domains decay approximately linearly in time, with a decay rate determined, not by the domain size, but by the local arrangement of neighboring domains. This observation is counter to the simplest picture of phase boundary motion, in which domain walls move with a constant velocity (independent of environment) determined by the free energy difference between the two phases. We have modeled the effect of the mass transport requirement on the observed decay by solving the two-dimensional diffusion equation for the experimentally-observed configuration of 7x7 domains. We find that the (7x7) domain decay is indeed limited by the supply of the additional material to the boundary. Detailed comparison of the diffusion model with experiment suggests the surprising result that the terrace (rather than surface steps) acts as the primary source of the additional atoms required for the (7x7) to (1x1) conversion. This model reproduces the simultaneous decay of all islands in the field of view with only one adjustable parameter.

11:00am **SS2+EM+NS-ThM9 The Motion of Atomic Steps on Ultra-Flat Si(111)***, **P. Finnie**, Y. Homma,* NTT Basic Research Laboratories, Japan

The flattest silicon surfaces are typically made up of terraces of a low index crystal plane connected by atomic steps. We have studied sublimation and growth on ultra-flat Si(111) substrates@footnote 1@ which have (111) terraces of up to 50 microns in width separated by monoatomic steps. The motion of atomic steps is revealed in time lapse movies made by in situ scanning electron microscopy. When samples are heated to high temperatures (about 1000°C) the surface erodes in a step-flow mode: steps retreat in an orderly fashion, one after the other. Since new terraces are nucleated when step spacings exceed a temperature dependent critical length, the spacing between steps is tunable. Measurements of step velocities as a function of terrace width compare well with theory. The interactions between steps are observed directly by forcing steps to collide@footnote 2@ either destructively, in which opposing steps annihilate, or constructively, in which steps moving in tandem coalesce into double (or triple, or larger) steps. We also studied molecular beam epitaxy in this high temperature regime. Using an electron beam to supply a flux of elemental silicon, desorption is countered and growth occurs in the step-flow mode. Remarkably flat grown surfaces can be obtained in this way since step-flow growth maintains an ultra-flat profile. Monoatomic height island nucleation can also be observed, with circular islands growing to diameters of tens of microns, seamlessly merging with neighboring terraces as the steps collide destructively. @FootnoteText@ @footnote 1@ Y. Homma, H. Hibino, T. Ogino, and N. Aizawa, Phys. Rev. B 55 (1997) R10237 @footnote 2@ P. Finnie and Y. Homma, Phys. Rev. Lett. 82 (1999) 2737.

11:20am **SS2+EM+NS-ThM10 Novel Growth Behavior of Ge on Pb Covered Si(111) Surface***, I.S. Huang,* Academia Sinica, ROC*; T.C. Chang,* Academia Sinica, ROC, Republic of China*; **T. Tsong**,* Academia Sinica, ROC

A surfactant can modify the growth behavior of a system to our advantages. We report discovery of a novel growth behavior in a Pb-layer promoted growth of Ge on Si(111). For this system, not only can Ge atoms grow on Si(111) surface layer by layer for many layers, but the growth behavior is contrary to traditional nucleation and growth theory and most experimental results in epitaxy. This growth is not governed by the reaction-limited-aggregation (RLA) process at low temperature as has been found in traditional epitaxy. The most interesting feature we find is that a compact-to-fractal island shape transition occurs when the sample temperature is increased, or the deposition flux is decreased. In traditional epitaxy, fractal growth occurs by diffusion-limited-aggregation (DLA) at low temperatures, thus fractal growth will disappear as the sample temperature is raised to the extent that step edge diffusion can occur. Our observation demonstrates that fractal islands can also be grown by RLA, and the importance of reactions in aggregation of Ge atoms in this system. Earlier theories neglect the reaction processes which may be acceptable for metal-on-metal systems, but are not good enough for other systems. Our result points to a need to develop a more complete nucleation theory where both diffusion and reaction are properly taken into account.

11:40am **SS2+EM+NS-ThM11 The Growth of High Density, Small Ag Islands at the Si(111)7x7 Surfaces with Adatom Defects***, **H. Hirayama**, H. Okamoto, K. Takayanagi,* Tokyo Institute of Technology, Japan

We studied the growth of Ag islands on the Si(111)7x7 surfaces with missing adatoms. The missing adatoms were created by 0.5keV Ar ion bombardment. Ag atoms were deposited on the surfaces at room temperature. The growths were observed by using scanning tunneling microscope (STM). At the Si(111)7x7 surface of no missing adatoms, several half unit triangular cells of the 7x7 reconstruction changed their contrast to be bright in the initial stage of the Ag deposition . Then, at the coverage above 0.03 monolayer (ML), each bright triangular cell changed to a bright spot. With the coverage, the number of bright spots increased, and occasionally two spots in neighboring cells kissed. At 0.8ML, the surface was covered by the two-dimensional (2D) percolating network of kissing spots. On the network, three-dimensional (3D) Ag islands grew. Meanwhile, at the Si(111)7x7 surfaces with missing adatoms, the bight spots appeared at the very early stage of the Ag deposition. The spots appeared as to avoid missing adatom sites. This resulted in an imperfect 2D network; the connection of kissing spots were cut into pieces here and there. On the imperfect 2D network, 3D islands grew above 0.7ML. At the stage of the 3D island growth, the missing adatom sites of the underlying 2D network was never filled up. However, we found strong dependence of the size and density of the 3D islands on the number of missing adatoms at the starting surfaces. With an increase of missing adatoms, the size of the islands decreased, while the density increased dramatically. The effects of the missing adatoms on the 3D Ag islands growth were attributed to the substantial increase of the super saturation and the decrease of the diffusion constant of Ag atoms on the imperfect 2D network.

Surface Science Division
Room 604 - Session SS3+AS+NS-ThM

Novel Surface Probes & Technique Enhancement

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

8:20am **SS3+AS+NS-ThM1 Determination of Sticking Probability and Transition State Energy by Line-of-Sight Detection: Halocarbons on Cu(111)***, **A.S.Y. Chan**, C.A. Clifford, R.G. Jones,* University of Nottingham, UK

We have used a new technique, Line-of-Sight Sticking Probability (LOSSP) to study the reactions of chloroform and 1-bromo-2-chloroethane (BCE) on Cu(111). The sticking probability measurements were made by applying a thermally randomised pressure of the halocarbon above the surface and detecting the reflected flux as a narrow beam of molecules flying in line-of-sight from the centre of the sample surface to the mass spectrometer.@footnote 1@ The general reaction undergone by both halocarbons on the copper surface is: M(gas) -> M(phys) [1] M(phys) -> M(gas) [2] M(phys) -> chemisorbed halogens + gas phase product [3]. By measuring the sticking probability as a function of temperature, we are able to obtain the energies of the transition state M(phys) towards decomposition, which for the non-activated adsorption system of BCE on Cu(111) is ~13 kJ/mol below zero, and for the activated adsorption of chloroform on Cu(111) is ~4 kJ/mol above zero. (Zero energy is defined as the energy of the molecule at an infinite distance from the surface. @FootnoteText@ @footnote 1@ R G Jones and C J Fisher; Surface Science 424 (1999)127.

8:40am **SS3+AS+NS-ThM2 Demonstration of Angle Resolved Auger-photoelectron Coincidence Spectroscopy from a Solid: First Results from the Cu(111) Surface***, **D.A. Arena**, R.A. Bartynski,* Rutgers University*; D. Cvetko, L. Floreano, A. Morgante, F. Tommasini,* Laboratorio Nazionale TASC-INFM, Italy*; A. Attili, A. Ruocco, G. Stefani,* Universita' di Roma, Italy*; L. Marassi, P. Luches,* Universita' di Modena, Italy*; S. Iacobucci,* CNR-IMAI, Montelibretti, Italy

We report the first successful angle-resolved Auger-photoelectron coincidence spectroscopy (AR-APECS) measurements from a solid. These measurements were made at the ALOISA beamline at the ELETTRA synchrotron radiation center in Trieste, Italy. This novel analysis chamber is equipped with seven hemispherical electron energy analyzers mounted on two independent rotatable frames; the arrangement allows for the efficient exploration of different kinematical conditions for the emitted pair of electrons. We measured the angular distribution of Cu L@sub3@VV Auger electrons from the Cu(111) surface in coincidence with Cu 2p@sub 3/2@ photoelectrons emitted at selected angles; these angles correspond to maxima and minima in the photoelectron diffraction (PED) pattern. When the 2p@sub 3/2@ core level is at a PED maximum, the Auger pattern is indistinguishable (within statistics) from the noncoincidence distribution. In contrast, if the 2p@sub 3/2@ photoelectrons are at a PED minimum, the coincidence Auger angular distribution shows additional structure as compared to the noncoincidence pattern. This observation may arise because the two coincidence conditions access different intermediate states. The effects of the lattice may be more pronounced in the Auger angular pattern collected in coincidence with photoelectrons on the PED maximum while the Auger angular distribution acquired in coincidence with the photoelectrons on the PED minimum may exhibit more "atomic-like" behavior. Alternatively, the difference may be a consequence of different probing depths on and off the PED maximum, and hence the sampling of different scattering sites. Experiments to discriminate between these possibilities are currently underway. This work is supported by NSF-DMR 98-01681 and NATO-CRG 97-0175.

9:00am **SS3+AS+NS-ThM3 Multiple Atom Resonant Photoemission: A New Tool for Determining Near-Neighbor Atomic Identities and Bonding***, **A.W. Kay**,* UC Davis and LBNL*; E. Arenholz,* LBNL and UC Berkeley*; B.S. Mun,* UC Davis and LBNL*; J. Garcia de Abajo,* LBNL*; C.S. Fadley,* UC Davis and LBNL*; R. Denecke, Z. Hussain, M.A. Van Hove,* LBNL

A newly discovered resonance photoemission process between neighboring atoms in multielement samples will be presented. Experimental evidence for the effect and possible applications will be considered. In several metal oxides, including MnO, Fe2O3, and La0.7Sr0.3MnO3, we have observed an enhancement in the core-level photoelectron peak intensity associated with one element in the sample (e.g. O 1s) while the excitation energy is tuned through an energetically deeper absorption edge of a second element (e.g. Mn 2p or Fe 2p or La 3d). At the edges of this second element, a 40-100% enhancement in the peak intensity (as an area above inelastic background) of the first element is observed. Furthermore, this peak intensity enhancement exhibits a dependence upon photon energy that closely, but not identically, follows the x-ray absorption coefficient of the second atom. This is evidence of an interatomic or multi-atom resonance photoemission (MARPE) process, that is related to but distinctly different from the much-studied intraatomic or single-atom resonance photoemission (SARPE). Theoretical calculations based on extensions of previous intratomic resonance models have yielded encouraging agreement with our experimental results. The MARPE effect is expected to provide a direct method for determining the atomic identities (atomic numbers) of near-neighbor atoms to the excited atom, as well as providing a new technique for studying bonding and magnetism in molecules, at surfaces,buried interfaces, and perhaps bulk materials provided that secondary fluorescence detection of the resonance can be utilized.@footnote 1@ @FootnoteText@ @footnote 1@ This work was supported by the U.S. Department of Energy, Office of Energy Research, Basic Energy Sciences Division, Materials Science Division, and the Miller Institute (Berkeley).

9:20am **SS3+AS+NS-ThM4 Incident Beam Diffraction in Electron Stimulated Desorption***, **M.T. Sieger**, G.K. Schenter, T.M. Orlando,* Pacific Northwest National Laboratory

The use of electron beams to remove surface-bound atoms and molecules (electron-stimulated desorption, or ESD) is a topic of interest for many disciplines, from semiconductor device processing to astrophysics. We have been studying the role of scattering and diffraction of the incident electron in the initial state of the desorption process. We report calculations and experiments demonstrating that total ESD yields show fine-structure with incident electron direction, consistent with quantum-mechanical scattering and interference of the electron in the initial state of the desorption process. In a time-independent picture interference of the incident plane wave with waves scattered from the crystalline lattice forms an electron standing wave (ESW), having spatially localized maxima and minima in the incident electron density. Whether a particular point on a surface experiences a maximum or minimum depends on the wavelength of the electron, the direction of incidence relative to the crystal axes, and the locations of nearest neighbor atoms. Since the probability of excitation is proportional to the incident electron density at or near the site of the "absorber" atom (the site of the inelastic scattering event), the total ESD rate should depend upon the local atomic structure and the k-vector of the incident wave. The total desorption yield, when measured as a function of incident direction at constant energy, shows oscillations with the symmetry of the absorber bonding site. Since every inequivalent atomic bonding site has a unique pattern of oscillation electron standing wave stimulated desorption (ESWSD) measurements can in principle uniquely determine the bonding geometry of the absorber. We present experimental measurements for chlorinated Si surfaces.

9:40am **SS3+AS+NS-ThM5 Direct Atomistic Observation of Structural Dynamics in Surfaces and Interfaces by Time-Resolved High-Resolution Transmission Electron Microscopy***, **T. Kizuka,*** Nagoya University and Japan Science and Technology Corporation, Japan **INVITED**

Atomic processes of mechanical interaction and gas-phase epitaxial growth were directly observed in situ by time-resolved high-resolution transmission electron microscopy at spatial resolution of 0.1 nm and time resolution of 1/60 s. Nanometer-sized tips of gold and silicon approached, and were contacted, bonded, deformed and fractured inside a 200 kV electron microscope using a piezo-driving. Contact boundaries of a few atomic columns width in gold, silicon/silicon-oxide/silicon tunnel junctions, and quantum dots of silicon/gold-cluster/silicon were produced.@footnote 1@ A few layers near the surfaces and contact-boundaries were responsible for the bonding and separation processes. Atomic scale contact or non-contact type surface-scanning similar to that in scanning probe microscopy was performed by the same method.@footnote 2@ The mechanical removal of one atomic layer was also demonstrated.@footnote 3@ New kinds of atomic scale mechanical tests, such as friction test, compressing, tensile and shear deformation tests were proposed. Gold was vacuum-deposited on (001) surfaces of magnesium oxide inside the electron microscope. Atomic process of epitaxial growth was in-situ observed cross-sectionally. Various types of growth phenomena, such as 'embryo' formation, structural fluctuation, repeated process of truncation and construction of a corner in one gold cluster, secondary nucleation and coalescence, were analyzed in real-space.@footnote 4@ @FootnoteText@ @footnote 1@T. Kizuka, Phys. Rev. Lett., 81 (1998) 4448. @footnote 2@T. Kizuka et al., Phys. Rev., B55 (1997) R7398. @footnote 3@T. Kizuka, Phys. Rev. B57 (1998) 11158. @footnote 4@T. Kizuka et al., Phys. Rev. B56 (1997) R10079.

10:20am **SS3+AS+NS-ThM7 Ionization Mechanisms of Water in High Interfacial Electric Fields***, **D.L. Scovell**[1],* University of Washington, U.S.A*; V.K. Medvedev, C.J. Rothfuss, E.M. Stuve,* University of Washington

High surface fields (Ã1 V/Å) drive many important processes, such as electrochemistry and field emission. The behavior of water in these fields is important because water is the primary component in electrochemical processes and a major contaminant in the vacuum surrounding field emitter arrays in flat panel displays. It is usually assumed that water amplifies the field at the electrode surfaces, but little is known about how water affects the electric field distribution. Field emitter tips lend themselves to the study of the dielectric properties of water because they produce fields as high as 5 V/Å. To better understand the effect of high electric fields on water, numerical analyses have been conducted to model the electric field distribution around a water-covered emitter tip. The calculations include the field-dependence of the relative permittivity of the water adlayer. The model predicts that the dominant field occurs at the vacuum interface in thin water layers and at the metal surface in thick layers. In very thick layers the field at the tip surface is predicted to be greater than the applied electric field. This response is analogous to that assumed for a traditional electrode/electrolyte interface. Experiments have been conducted to verify the predicted trends for thin water layers. In these experiments water was adsorbed onto a platinum field emitter tip under field-free conditions in ultrahigh vacuum. Ionization was examined by isothermal ramped field desorption (RFD) performed as a function of temperature and water layer thickness. The experimental results are consistent with the predicted trends. This work was supported by the Office of Naval Research.

10:40am **SS3+AS+NS-ThM8 Free Electron Laser Nanospectroscopy Interface Applications***, **G. Margaritondo,*** Ecole Polytecnique Fédérale, Switzerland*; A. Cricenti,* Consiglio Nazionale delle Ricerche, Italy*; N.H. Tolk,* Vanderbilt University*; R. Generosi, P. Perfetti,* Consiglio Nazionale delle Ricerche, Italy*; I.D. Aggarwal,* U.S. Naval Research Laboratory

We present the first result of a major effort to investigate the lateral fluctuations of properties of solid interfaces on a microscopic scale. The key elements were the use of a small-tip optics fiber and its coupling with a scanning module; in this way, we achieved and verified the condition of near-field microscopy -- including a lateral resolution much below the wavelength value. Our discussion includes a presentation of the first scanning near-field optical microscopy images obtained with a free electron laser infrared sources and data on small and microscopic-scale fluctuations of semiconductor interface barriers.

11:00am **SS3+AS+NS-ThM9 Imaging and Charge Transport Measurements using Dual-Probe Scanning Tunneling Microscopy***, **H. Grube**, J.J. Boland,* University of North Carolina

Scanning tunneling microscopy has evolved into a valuable tool for the study of semiconductor and metal surfaces. However, the single probe geometry of STM limits its application to local and static measurements of the local density of states.@footnote 1@ Incorporation of a second electrically and mechanically independent STM tip within nanometers of the first enables measurements of surface properties that conventional STM cannot perform.@footnote 2,3,4@ Our DP-STM has been characterized by placing both tips in close proximity on a sample surface and obtaining images from each tip showing its local surface environment and the other probe. We discuss the challenges encountered of DPSTM and the feasibility of charge transport measurements on a variety of systems including carbon nanotubes. @FootnoteText@ @footnote 1@ G. Binnig et al., Phys. Rev. Lett., 49 (1), 57 (1982)@footnote 2@ Q. Niu, M. C. Chang and C. K. Shih, Phys. Rev., B 51 (8), 5502 (1995)@footnote 3@ J. M. Beyers and M. E. Flatte, Phys. Rev. Lett., 74 (2), 306 (1995)@footnote 4@ J. M. Beyers and M. E. Flatte, J. Phys. Chem. Solids., 56 (12), 1701 (1995)

11:20am **SS3+AS+NS-ThM10 The Miniature Cylindrical Mirror Analyzer: A New Tool For Surface Analysis***, **K. Grzelakowski,*** Focus Polska Sp. Z o.o., Poland*; M.S. Altman,* Hong Kong University of Science and Technology, P.R. China

The design and performance of a new miniature cylindrical mirror analyzer (CMA) are presented. The CMA comprises outer and inner cylinders, integral on-axis electron gun, and detector system consisting of ring aperture and channeltron, all mounted on a 2.75" flange. Entrance angle, sample-to-detector distance, and polar cone angle were chosen, in consideration of second order focussing effects, that optimized analyzer transparency and resolution. Fringe field correction at the ends of the CMA

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

is made by means of six rings precisely separated by sapphire insulators. The electron gun is a one-lens electrostatic system equipped with XY-deflector for beam adjustment and scanning. A CeB6 low temperature cathode operating at up to -2.0keV delivers emission current up to 100 mA. The energy range of analyzed electrons can be varied between 0 eV to 2.0 keV. The flange mounting also incorporates a high precision Z-motion for optimization of the working distance. The control electronics and software permit operation of the instrument in pulse and phase sensitive detection modes. Results obtained for a W(001) surface with this new miniature CMA demonstrate an energy resolution of 0.08%, which is comparable to larger 6" and 8" flange mounted instruments. The very small size of the mini-CMA permits its use in small or crowded ultra high vacuum chambers or where only 2.75" ports are available, thereby increasing flexibility in surface analysis.

11:40am **SS3+AS+NS-ThM11 Investigations of Surface Reactions on Thin Film-Supported Catalysts Using Microhotplate Arrays***, R. Walton, R. Cavicchi,* ***S. Semancik,*** *M. Class, J. Allen, J. Suehle,* National Institute of Standards and Technology

This presentation describes the use of microhotplate arrays and electrical measurements for efficiently investigating surface reactions on supported metal catalysts under varied temperature and gas exposure conditions. Each ~100 µm x 100 µm microhotplate platform used in our work includes functionality for rapid control and measurement of film temperature (thermal time constant ~ 1 ms) and for probing of gas-induced changes in a film's electrical properties. Arrays of individually addressable microhotplates are well suited for directly comparing catalytic layers of different composition, loading, and degree of dispersion. The results we present are relevant to both gas sensing and catalysis. Specifically, four-element arrays were used to evaluate reactions on Pt, Pd, and Cu catalyst particles (formed by annealing 25-100 Å layers) supported on tin oxide. Electrical conductivity was used to monitor changes in the electron density of the thin film catalysts caused by surface reactions in air of H@sub 2@, CO and CH@sub 3@OH, respectively, at film temperatures ranging from 20 to 500 °C. Each of the catalysts interacts with these reactants in air to produce changes in film conductivity that we relate to factors including surface oxygen concentration, reaction rates, catalyst loading, and catalyst fouling. As a further example of this approach, we also illustrate the use of microhotplates to explore the conditions of thermal cycling and partial pressures under which CO oxidation oscillations occur on Pt particles supported on SnO@sub 2@.

Thin Films Division
Room 615 - Session TF-ThM
Nanophase Thin Films

Moderator: J.S. Zabinski, Air Force Research Laboratory

8:20am **TF-ThM1 Thin Films from Slow and Energetic Cluster Impact***,* ***H. Haberland,*** University of Freiburg, Germany **INVITED**

An intense beam of clusters can be produced by first sputtering atoms into an argon atmosphere and then forming the clusters into a beam. Deposition rates of about 5 ML are observed for clusters between 1000 and 12.000 atoms of all metals tried so far (Ag, Al, Cu, Co, Mo, Ti, TiN, Pd) as well as for Si. Up to one third of the beam can be charged, so that an intense beam of cluster ions can be produced. Mass spectroscopy is used to determine the cluster size. Several examples will be discussed; e.g. Co clusters embedded in a Ag matrix for magnetic applications, Ag clusters in a SiC matrix for a two-dimensional conductor, etc. If the clusters impinge on the substrate with high kinetic energy (up to 30.000eV) they are deformed on impact and form a well adhering, smooth thin film. Unusual properties are observed: e.g. golden TiN films produced at room temperaturs, or well adhering metal films on Teflon, etc. Molecular Dynamics simulation are used to explain these unusual properties.

9:00am **TF-ThM3 Spark-Processing - A Novel Technique to Prepare Light-Emitting, Nanocrystalline Silicon Films***,* ***R.E. Hummel,*** University of Florida **INVITED**

Scientists are constantly searching for new processing techniques which are capable of modifying the properties of materials. This could yield alternative characteristics that may lead eventually to new consumer products or, more importantly, provide a better understanding of nature. Such a new technique is spark-processing, which has been shown to change remarkably the optical properties of silicon (and other materials). Specifically, spark processing (sp) creates a substance which transforms Si into a strongly photo-luminescing and cathodoluminescing material (in contrast to ordinary Si which is not light emitting). The resulting material is extremely stable against high temperature annealings, HF etching, and laser irradiation. The emission wavelengths range from violet to green to red, depending on the processing parameters. Further, sp-Si is ferromagnetic (compared to conventional Si which is diamagnetic). A new photoresitive device has been created from sp-Si which, upon impingement of light, increases or decreases its resistivity depending on geometric variables. Sp-Si is produced by high frequency, high voltage, low current electric pulses which are applied for a short time between a Si substrate and a counter electrode.

9:40am **TF-ThM5 Interesting Properties of Nanophase Films Deposited from a High-rate, Nanoparticle Beam***,* ***F.K. Urban III,*** *A. Khabari, A. Hosseini-Tehrani, P. Griffiths,* Florida International University

Nanophase thin films have been deposited by sputtering target material into a chamber designed and operated to promote condensation of the sputtered species into nanoparticles. Flowing argon and helium gas are used to sputter and assist condensation. Particle size and numbers depend on the nucleation rate, condensation rate, and time available for these processes. Films have been deposited from copper, cobalt, molybdenum, and composite copper-cobalt targets. The work to be reported here explores soft-landed nanoparticle films using no acceleration. The soft landed films are porous with nanocrystalline structure from about 5 to 10 nm crystallites. Properties of films are different from bulk and film literature values. The change in film structure with acceleration will be reported. SEM, TEM, AES, RBS, and AFM results will be presented.

10:00am **TF-ThM6 Simulation of Fundamental Physical Phenomena in the Deposition of Nanophase Thin Films using a Sputtering Based Source***, F.K. Urban III,* ***A. Hosseini-Tehrani****, A. Khabari, P. Griffiths,* Florida International University

Recently, nanophase thin films have been deposited by sputtering target material into a chamber designed and operated to promote condensation of the sputtered species into nanoparticles. Interesting optical and magnetic properties has been reported for these films. It has been recognized that quantum size effects are most consistent with observed data. The structure of the film and the grain size determines the film properties. In this work, the classical nucleation theory has been used to understand the processes involved in the nucleation and condensation of the particles. A detailed analysis of the nanoparticle beam energy has been carried out by deflecting, accelerating the beam and comparing the experimental data with simulations by SIMION computer code. Results of simulations and comparison to measuremnts and to the resulting depositd films will be presented.

10:20am **TF-ThM7 Deposited Porous Silicon on Insulator Substrates***, A.K. Kalkan, S.H. Bae, H. Li,* ***S.J. Fonash,*** The Pennsylvania State University

High porosity crystalline Si thin films have been directly deposited using a high density plasma approach at temperatures as low as 100°C. These films exhibit the same unique properties, such as visible luminescence and gas sensitivity, that are seen in electrochemically etched Si (i.e., porous Si). The ultimate advantage of our low temperature direct deposition approach is that now porous Si films can be obtained on any substrate including plastics. XRD identifies our films, deposited by ECR-PECVD, as crystalline with no preferential orientation. TEM shows our as-deposited porous Si films consist of a periodic array of uniformly sized rodlike columns normal to the substrate surface in a void matrix. A typical rod diameter is 80 Å and a typical rod separation is 30 Å. Unlike other previously obtained columnar films, these rodlike columns are not tapered but have a constant diameter. We have demonstrated this structure is fully controllable and have varied the porosity up to ~80% by varying the deposition conditions. We have also found that the porosity can be further increased by reducing the diameter of the Si columns by hydrogen ECR-plasma etch exposures after deposition. Red and orange photoluminescence has been observed from our high porosity films. Furthermore, a large and fast conductivity response to certain vapor or gas ambients has been found. In particular, in the case of humidity, a weak response was found up to a threshold humidity level. Above this level a steep exponential increase in conductivity of 3-4 orders of magnitude was observed. The onset of this steep increase was found to occur at higher humidity levels as the porosity is increased. A saturation is observed at relative humidity levels above 75%. Sensitivity for acetone and isopropyl alcohol was observed also for films in the higher porosity range. This implies the sensitivity for larger molecules may be enabled by increasing the void size.

10:40am **TF-ThM8 Optical Properties of Chiral Thin Film Nanostructures and Composites**, ***S.R. Kennedy***, *J.C. Sit, M.J. Brett,* University of Alberta, Canada

We have fabricated porous, chiral thin films with distinct helical nanostrucutures of dimension 300nm pitch and 100nm separation. The geometry of these microstructures can be easily controlled by careful substrate motion using the GLancing Angle Deposition (GLAD) technique.@footnote 1@ Because of their nanometer size scale, these helices give rise to optical phenomena, such as the wavelength specific rotation of linearly polarized light, or optical activity. Analysis of films has found that optical properties are functions of film material and thickness as well as helical pitch and radius. All of these characteristics can be accurately controlled during the deposition process to tailor the film's properties to the desired wavelength regime and rotatory power. For example, we have measured a peak rotation of 2.0° at a wavelength of 480nm when polarized light is incident normal to the plane of the film. The porosity of GLAD thin films has also allowed us to fill gaps surrounding the nano-helices with fluids to enhance the film properties. By filling the films with substances of varying indices of refraction, we were able to modify the rotational effect. In addition to filling with non-active fluids, we investigated the effect of combining optically active nematic liquid crystals with our chiral films. @FootnoteText@ @footnote 1@Robbie, K., & Brett, M. J., Nature, v13, 616 (1996).

11:00am **TF-ThM9 Solid State Electrochromic Devices for Thermal Emittance Control**, ***C.L. Trimble***, *E. Franke, M.J. DeVries,* University of Nebraska, Lincoln; *J.S. Hale,* J.A. Woollam Company; *J.A. Woollam,* University of Nebraska, Lincoln

Thin films of crystalline Li@sub x@WO@sub 3@ (0@<=@ x @<=@ 0.5) allow modulation of IR reflectance within the spectral region from 2 to 30µm depending on the amount of inserted Li ions. Weakly crystalline or amorphous NiO thin films maintain a highly IR transparent state upon Li intercalation. By changing the reflectance of the Li@sub x@WO@sub 3@ layer in contrast to the supporting device layers, electrochromic devices with variable IR emittance can be built. We study a solid state electrochromic device consisting of a five layer stack on glass substrates with a layer sequence: electrode/a-Li@sub x@NiO/Ta@sub 2@O@sub 5@/c-Li@sub x@WO@sub 3@/electrode. The layers are deposited by reactive dc and rf magnetron sputtering at various substrate temperatures, total gas pressures, and oxygen partial pressures, in high-vacuum conditions. Lithium is electrochemically inserted into WO@sub 3@ using a 1N LiClO@sub 4@/propylene carbonate solution. WO@sub 3@, NiO, and Ta@sub 2@O@sub 5@ are deposited on glass/ITO, or Si substrates. The structural and optical properties of the as-deposited thin films, as well as the Li intercalated WO@sub 3@ and NiO single layers are investigated by XRD, AFM, and IR ellipsometry, in-situ and ex-situ UV-VIS ellipsometry, and IR reflectance measurements. The WO@sub 3@, NiO, and Ta@sub 2@O@sub 5@ thin film optical constants are obtained in the IR and VIS spectral region. Electrochromic devices are designed with consideration of the single layer thin film properties. To predict the device IR emittance modulation performance IR reflection and transmission of the colored and bleached devices are measured. The device switching and memory behavior are tested. The Li depth distribution within the electrochromic devices is investigated by secondary neutral mass spectroscopy (SNMS).@footnote 1@ @FootnoteText@ @footnote 1@ Research supported by BMDO contract #DSAG60-98-C-0054 and NASA Epscor Research Center contract #NCC5-169.

11:20am **TF-ThM10 Correlation Between Phase Constituency and Near Ultraviolet Optical Absorption in Nanophase Titania Films**, *J.D. DeLoach, G. Scarel,* University of Wisconsin, Milwaukee; ***C.R. Aita,*** University of Wisconsin, Milwaukee, US

Titania forms coexisting nanocrystalline and vitreous structures in films grown at room temperature. This study's goal is to correlate fundamental optical absorption edge characteristics with nanophase constituency of titania films. Films with coexistent rutile, anatase, and vitreous constituents were sputter deposited onto fused silica, and post-deposition air-annealed at 700 and 1000 @super o@C to affect phase changes. X-ray diffraction was used for phase identification, and UV spectrophotometry was used to determine the optical absorption coefficient at the onset of interband transitions. The absorption coefficient was modeled using the coherent potential approximation, with Gaussian site disorder introduced into the valence and conduction bands of a perfect virtual crystal. Two parameters of the disordered crystal were defined: the optical band gap, E@sub x@, and the slope of absorption edge, E@sub o@. The results are discussed in terms of two extreme cases: (1) Films containing a large rutile volume fraction (0.70-1) share a rutile virtual crystal, with E@sub g@=3.22 eV. Data for these films were combined with single crystal data to develop an expression interrelating E@sub g@, E@sub x@, and E@sub o@. This expression is applicable to any structure with a rutile virtual crystal. The relationship between structural disorder (i.e., volume fraction of vitreous material) and electronic disorder (i.e., E@sub o@), is consistent with the CPA model. (2) Films with a small rutile volume fraction (0.02-0.17), and hence a large anatase+vitreous component, share a non-rutile virtual crystal, with E@sub g@=3.41 eV. The effect of increasing the structural disorder (i.e., rutile volume fraction), in these films is to shift E@sub x@ to lower values, which is consistent with the CPA model. Furthermore, anatase and vitreous components were modeled using the same non-rutile virtual crystal, indicating these structures have a common short-range order in these films.

Vacuum Technology Division
Room 610 - Session VT-ThM

Outgassing, Leaks, and Mass Flow Controllers

Moderator: W. Weed, Sandia National Laboratories

8:20am **VT-ThM1 A Comparison of Outgassing Rates from Stainless and Carbon Steels**, ***H.F. Dylla,*** Thomas Jefferson National Accelerator Facility; *W.R. Blanchard,* Princeton University

Various types of stainless steels (ANSI type 300 series) are the most commonly used materials for the construction of high and ultrahigh vacuum vessels and associated vacuum hardware. As a result of this widespread use, numerous outgassing studies of stainless steels have been published in the literature. The available information on outgassing from carbon steels is relatively meager. Carbon steels are usually not considered for use in high vacuum systems because of the propensity for corrosion (oxidation) in ambient environments and the assumption that standard surface preparation techniques would be less effective on carbon steels in comparison to 300 series steels. During consideration of a number of vacuum applications of carbon steels we reviewed the outgassing literature and found that an often quoted measurement significantly overestimates the outgassing from properly cleaned material. We describe outgassing measurements we have performed on both types of steel in order to get a direct comparison of the materials on the same apparatus and using the same surface preparations techniques. Results show that the short-term (<100 hr) outgassing rates from clean carbon steel are only a modest factor (times two to four) larger than from similarly prepared stainless steel. The increased outgassing rate appears to be in direct proportion to the passivation oxide layer thickness. @FootnoteText@ This work was supported by US DOE Contract No. DE-AC02-76-CH-03073.

8:40am **VT-ThM2 Experiments with Thin-Walled Stainless Steel Vacuum Chamber**, ***V. Nemanic,*** Institute of Surface Engineering and Optoelectronics, Slovenia; *J. Setina,* Institute of Metals and Technology, Slovenia

The application of reasonably thin stainless steel wall was suggested recently as alternative approach in construction of UHV chambers, since the hydrogen outgassing rate can be decreased to the level required to reach UHV and EXV much easier. Experimental stainless steel chamber (AISI type 304, volume 13 l) with uniform wall thickness (0.6 mm) has been constructed. It was equipped with a miniature ion-getter (IG) pump and spinning rotor gauge (SRG) thimble. The chamber was pumped down and initially degassed by moderate bake-out (2.5h, 150 deg.C) by a turbomolecular pump system. Gas accumulation method was applied for determination of outgassing rate q@sub out@ and total amount of released gases using capacitance manometer during pump down and SRG after the chamber was sealed-off. The initial q@sub out@ at room temperature after initial degassing was in the range of q@sub out@=10@super -12@ mbar l s@super -1@cm@super -2@ with a tendency of slight decrease with time. Thermal dependence of outgassing rate was determined from SRG measurements in the temperature range from 19 to 50 deg. C over several days with ability to extract the offset value by means of IG pump. The bake-out of the chamber was repeated for 72h at 200 deg. C which lead to the decrease of outgassing rate to one tenth of the initial value. The results show the benefit of using a moderately thin wall and agree well with a model of recombination limited hydrogen outgassing from stainless steel. @FootnoteText@ B.C.Moore: Atmospheric permeation of austenitic stainless steel, J.Vac.Sci.Technol., A16(5), 3114-3118, 1998 V.Nemanic,T.Bogataj: Outgassing of a thin wall stainless steel chamber, Vacuum, 50, 3-4, 431-437, 1998

9:00am **VT-ThM3 Review of Models for the Outgassing of Water Vapor from Metallic Surfaces***, **B.B. Dayton,*** Consultant **INVITED**

The variation of outgassing rate with pumping time for water vapor from unbaked metal surfaces has been shown by several authors to depend on the ratio of pumping speed to exposed surface area, the time of initial exposure to the atmosphere at a known humidity, the ambient temperature, the thickness and porosity of the oxide layer on the metal surface, and the pretreatment or conditioning of the surface. The outgassing behavior differs radically from that for plastics and elastomers, and many authors have attempted to explain this behavior on the basis of theoretical models for the molecular kinetics. These models will be reviewed and evaluated. The present author will suggest a new model based on rapid physical adsorption and desorption in the oxide layer, with heat of adsorption in the neighborhood of 10 kcal/mol (corresponding to two hydrogen bonds), during atmospheric exposure followed by a slower (low probability) transition from a physisorbed precursor state (with activation energy of about 5 kcal/mol corresponding to breaking of one of the hydrogen bonds) to a "weak chemisorption state'', involving rotation and wobble about the remaining single hydrogen bond until an exposed pair of electrons associated with the water molecule has been captured in the positive field of a nearby metal ion without necessarily breaking the hydrogen bond to the oxide ion. Outgassing then involves the desorption of the undissociated water molecule from this bound state to the gas phase with an energy of desorption ranging from 20 to 30 kcal/mol.

9:40am **VT-ThM5 Measuring and Locating Internal Helium Leaks in the RHIC Insulating Vacuum System***, R. Davis,* Brookhaven National Laboratory, U.S.*; C. De La Parra,* ***H.C. Hseuh****, P. Mickaliger, D.J. Pate,* Brookhaven National Laboratory

The Relativistic Heavy Ion Collider (RHIC) uses superconducting magnets to bend and focus the high-energy particle beams. Strings of these magnets are enclosed in insulating vacuum cryostats up to 480 meters long. The cryostat vacuum must be 10@super -5@ Torr or less to minimize heat transfer from the ambient cryostat wall to the 4K magnet cold mass. There are over 25,000 in-situ welds of internal helium lines with a total weld length over 7 km. Helium leaks greater than 10@super -5@ std.cc/sec (ambient leak rate) in these welds were located and repaired. The methods of locating these leaks in the long cryostat volumes will be described. Smaller leaks were monitored during the cool down of the magnets. The correlation of the leak rates with the helium line temperature and pressure will be presented.

10:00am **VT-ThM6 Contraflow Leak Detectors with Improved Sensitivity Under High Helium Background Conditions****, **C. Dong,*** Old Dominion University*; G.R. Myneni,* Thomas Jefferson National Accelerator Facility*; G.A. Rooks,* Varian Vacuum Technologies

The leak detection sensitivity of the contraflow leak detectors is limited in general by its high operating pressure. Helium is known to be trapped in the fore pump of the leak detector and contributes to the large background signal particularly after leak checking large leaks (~1.0e-4 Pa. l/s). The trapped background helium can be effectively removed by purging the system with dry nitrogen. Such nitrogen purge is found to shorten the clean up period of leak detector by 90%. A novel method was developed to detect small leaks in large background helium signal. This method includes the lowering of pumping speed and adjustment of leak detector parameters such as the reduction of emission current and lowering the zero offset to minimize the background helium signal. We are able to leak check 3.0e-8 Pa. l/s and smaller leaks in a background signal of 4.0e-6 Pa. l/s of helium with 20 % accuracy. * This work was supported by U.S. DOE Contract No. DE-AC05-84ER40150 and Varian CRADA No. SURA-97-S002

10:20am **VT-ThM7 LIGO Beam Tube Component and Module Leak Testing***, **W.A. Carpenter**, P.B. Shaw,* Chicago Bridge and Iron Co.*; R. Weiss,* Massachusetts Institute of Technology*; L. Jones,* California Institute of Technology

LIGO (Laser Interferometer Gravitational-wave Observatory) is a joint project of the California Institute of Technology and the Massachusetts Institute of Technology funded by the National Science Foundation. The project is designed to detect gravitational waves from astrophysical sources such as supernova and the formation of black holes. The LIGO project constructed facilities at two sites in the U.S. Each site includes two perpendicular laser beam tube lines (each 4 km long) which join at one end to form an "L" shape. The beam tube is a stainless steel, ultra high vacuum tube which will operate at a vacuum of 1 x10@super -9@ torr or better. The beam tube was manufactured using a custom spiral weld tube mill and was manufactured with special emphasis on reduced outgassing rates. The integrity of the beam tube was assured by leak testing each component of the beam tube system prior to installation and then to leak test each 2 kilometer isolatable beam tube module after completion. This paper discusses the leak detection procedures used to leak test 16 km of 1.25 m diameter UHV beam tube used in the LIGO project. The beam tube was leak tested in four steps including leak testing fabricated tube sections, local leak testing of 250 mm diameter valve and valve nozzles, leak testing circumferential welds joining tube sections together and final leak testing of the installed beam tube module. The component leak testing included 800 tube sections which were 20 m long, 808 circumferential welds and 72 valved nozzles. Each component was tested to a sensitivity of better than 1x10@super -10@ atm. cc/sec of helium. The leak test of the 2 kilometer beam tube module would have been extremely difficult and expensive using standard helium leak detection techniques. Therefore, a method was developed utilizing a Residual Gas Analyzer (RGA) to measure the leak tightness of the two kilometer long modules. A method was also developed to utilize nine RGAs to locate any detected leaks.

10:40am **VT-ThM8 Low-flow Measurements Techniques for Calibrating Mass Flow Controllers***, **S.A. Tison**,* Millipore Corporation, U.S.A*; C. Ruppert,* Millipore Corporation

Many semiconductor processes require stable and known flow of a gas or multiple gases. Flows ranging from 100 slpm (7 x 10-2 mol/s) to 10 sccm (7 x 10-6 mol/s) are common. Primary standard flowmeters have been developed to measure these flows and are in common use.. The most common techniques include gravimetric and those based on volume displacement at constant pressure. Recently a significant number of processes are using much lower flows with flows as low as 0.1 sccm (7 x 10-8 mol/s) being required. Most of the traditional techniques for measuring gas flow are not well suited for measurements in this range. Becasue of this, process tuning and reproducability can be adversely affected by errors in the mass flow controllers which are induced by their calibration. Two of the most common instruments used for low-flow measurements , a constant volume flowmeter and a laminar flowmeter, were compared with a number of gases including nitrogen, hydrogen, and sulfur hexafluoride. The agreement of the techniques was generally within 0.5% over a range of 1 sccm (7 x 10-7 mol/s) to 10 sccm (7 x 10-6 mol/s) and somewhat worse for lower flows. The comparison data and attributes of these two types of standards is discussed.

11:00am **VT-ThM9 Dimensionless Parameters for Laminar Flowmeters***, **R.F. Berg**,* National Institute of Standards and Technology

Laminar flowmeters have strong advantages as transfer standards for measuring low flow rates of gases. Ideally, the difference between the flowmeter's entrance and exit pressures, P@sub 1@ and P@sub 2@, is that associated with viscous, creeping flow. One can then approximate the volume flow rate by the value Q@sub 0@ = @pi@R@super 4@(P@sub 1@-P@sub 2@)/(8@eta@L). This is the Hagen-Poiseuille relation which describes an incompressible fluid of viscosity @eta@ flowing through a capillary of circular cross-section with length L and radius R. In practice, the actual flow rate Q is described by the discharge coefficient C@sub d@=Q/Q@sub 0@. Achieving an accuracy of 0.1% requires a series of corrections to C@sub d@, each associated with at least one dimensionless parameter. Identifying the form of these corrections allows one to define useful dimensionless parameters. Important deviations of C@sub d@ from unity occur because the gas is compressible. A steady mass flow rate causes the volume flow rate to depend on position along the capillary. This corrects C@sub d@ by a factor proportional to (P@sub 1@+P@sub 2@). Furthermore, the additional pressure drop associated with the expanding gas adds to C@sub d@ a term proportional to the Reynolds number Re. Recent analysis of capillary viscometers by van den Berg and coworkers showed that the nonparabolic flow associated with the expanding gas increased the size of this term. Their result is used here to describe the performance of a laminar flowmeter. Dimensionless parameters incorporated in this correction include Re, the pressure ratio P@sub 2@/P@sub 1@, and the aspect ratio R/L. Other significant dimensionless parameters include the Mach number, the ratio of the gas's slip length to the capillary's radius, the Dean number characterizing centrifugal effects in a coiled capillary, and the correction terms in the gas's virial equation of state.

11:40am **VT-ThM11 Decay Rate of Photoresist Outgassing from Ion Implantation***, **A.S. Perel**, T.N. Horsky,* Eaton Corporation

Outgassing of hydrocarbons results from ion implantation into wafers covered with photoresist. Depending on the implant energy and current, the quantity of gas can be large and therefore high effective pumping speeds are important to minimize interference with the ion beam. We measured the time dependence of this outgassing to determine the rate that the outgassing decays. This information is relevant for design of implanter process chambers with rotating disks. The photoresist outgassing decay rate determines the geometry of the gas load, and can be used to determine pump placement and chamber design. The experiment involved a single photoresist wafer and 12 dummy wafers on a 13 pad disk. By measuring the collector current directly from the ion gauges we were able to time-resolve pressure measurements to better than 1 ms. Two pressure pulses were measured, the pulse that results from the implant and a pulse that results from the outgassing wafer passing the gauge. The relative difference in amplitude and time, as observed from two gauges, were used to calculate the outgassing decay rate. We reduce several data sets collected at different disk rotational speeds to fit a candidate model for the time-dependence and mechanism of photoresist outgassing.

Applied Surface Science Division
Room 6A - Session AS-ThA

Polymer Surfaces, Films, and Interfaces

Moderator: P.M.A. Sherwood, Kansas State University

2:00pm **AS-ThA1 Conformation and Orientation Effects in the XPS Spectra of Thin Polymer Films*, G. Beamson,*** Daresbury Laboratory, U.K., United Kingdom **INVITED**

The conformation and orientation of polymer chains at surfaces and in thin films can play an important role in determining the properties of technological systems, and may be different from the bulk polymer. Techniques such as GIXS, NEXAFS, AFM, infrared spectroscopy, ellipsometry and XPS are currently being used to investigate the arrangement of polymer chains at surfaces. Conformational effects in the XPS spectra of polymers are small, but advances in instrumentation over the past decade have increased their probability of detection. The search for conformational signatures requires careful measurements on well characterised polymers as a function of conformational change. Changes in conformation often accompany a change in crystallinity or physical state. Polymers suffer x-ray induced degradation during XPS which can mask subtle conformational effects. Hence time dependent studies are required to establish upper limits on x-ray exposure times such that degradation is not a concern. Differential charging can also mask subtle spectroscopic effects and good charge compensation is crucial for the detection of conformational signatures. Orientation effects in polymer systems can be probed by angle dependent XPS studies. A conformational signature in the C 1s spectrum of PET will be discussed and comparison of XPS and infrared data will be used to demonstrate faster conformational change at the surface than in the bulk when the polymer is annealed above Tg. Conformational signatures in the valence bands of PEG, PTMG and nylon 12 will also be described. Angle dependent XPS studies of orientation effects in molecular overlayers on PTFE tribological transfer films will be discussed. Functional group orientation effects in acrylic polymers will also be described.

2:40pm **AS-ThA3 Correlative XPS and FTIR Imaging Analysis of Polymer Blends*, J.E. Fulghum,*** *K. Artyushkova, A.C. Ferryman,* Kent State University*; J.L. Koenig,* Case Western Reserve University

Phase segregation in blends of poly(vinyl chloride) and poly(methyl methacrylate) has been evaluated through correlation of photoelectron and infra-red images and small area spectra. Polymer surfaces which are heterogeneous on the scale of microns can be characterized by XPS if both imaging and small area spectroscopy are utilized. Polymer compositions in the bulk phase are routinely evaluated using FTIR spectroscopy. In this study, we take advantage of recent advances in the imaging capabilities of both techniques to improve characterization of heterogeneous organic samples. Surface-specific chemical information was acquired using a Kratos AXIS Ultra photoelectron spectrometer, while phase-segregation in the bulk was studied using a Biorad Stingray FTIR microscope. Images of comparable spatial resolution are readily obtained, allowing for a more complete characterization of lateral and vertical phase segregation than is possible with a single spectroscopic technique. Core and valence band XPS determinations of polymer blend composition in phase-separated regions will be compared to results based on small-area FTIR spectra. This work has been partially supported by NSF DMR89-20147 and 3M.

3:00pm **AS-ThA4 Beam Induced Damage Effects in XPS Studies of Thin Organic Films*, H. Cohen,*** *R. Maoz, E. Frydman, J. Sagiv,* The Weizmann Inst. of Science, Israel

Beam induced irreversible effects are frequently overlooked in XPS studies of thin organic films, mainly because of limitations in self testing capabilities of the technique. Minimization of such effects requires elaborated experimental procedures, and a fundamental understanding of the dominant damage mechanisms. Aiming at this goal, a thorough study of X-ray induced effects in layered self assembled organic films has been conducted using a number of complementary techniques, additional to the in-situ XPS measurements. Chemical functions particularly sensitive to the X-ray radiation have been identified. Structural and chemical modifications are discussed as a function of the initial film composition, and their significance for potential applications is indicated.

3:20pm **AS-ThA5 Surface Analysis of Nitrogen Plasma-Treated Poly (ethylene-2,6-naphthalate) Films using XPS and Gas Phase Derivatization Reactions*, Y. Liu,*** *L. Gerenser,* Eastman Kodak Company

Nitrogen plasma-treatment is a very useful technique for modifying the surface properties of polymers, including adhesion, wettability and biocompatibility, through the introduction of nitrogen functional groups. This presentation will focus on the characterization of nitrogen plasma-treated poly (ethylene-2,6-naphthalate) films using conventional XPS and gas phase derivatization reactions in combination with XPS. The selectivity and yield of trifluoroacetic anhydride for primary amines, and trifluorotolualdehyde for secondary amines, were determined by reacting them with model compounds containing the nitrogen group of interest (e.g., primary and secondary amines, amides and nitriles). The quantity and depth distribution of primary and secondary amines for nitrogen plasma-treated PEN were evaluated as a function of gas composition (e.g, N@sub 2@, NH@sub 3@, and N@sub 2@O) and treatment conditions (power and pressure). Correlations were found between the plasma conditions and the resultant surface chemistries.

3:40pm **AS-ThA6 Quantitative Analysis of Functional Groups with TOF-SIMS*, T. Fladung,*** *D. Wolany, T. Gantenfort, L. Wiedmann, A. Benninghoven,* Universität Münster, Germany

The unique identification and quantitative analysis of functional groups from plasma treated polymer surfaces with XPS and TOF-SIMS is often difficult. In this case, derivatization and subsequent quantitative XPS is well-known for a number of important functionalities. We will show that the analysis of derivatization products with TOF-SIMS can extend the limited sensitivity of XPS by several orders of magnitude and, at the same time, be made quantitative by suitable calibration. After gas phase derivatization of hydroxide groups with trifluoroacetic anhydride (TFAA), the XPS results of monofunctional model polymers can be used as standards for the calibration of SIMS data. During TOF-SIMS analysis of the model polymers after derivatization, the intensity of a characteristic set of molecular ions containing fluorine is proportional to the concentration of OH groups as determined by XPS, and can thus be taken as a quantitative measure of the surface concentration of OH groups. For polypropylene and polycarbonate samples treated in an oxygen and argon plasma, respectively, the modified surfaces were derivatized with TFAA and analyzed with XPS and TOF-SIMS. The results were used to quantitatively distinguish the OH groups from other functionalities generated by the plasma such as carbonyl or carboxyl groups. Principal component analysis was used for the comparison of SIMS spectra before and after derivatization. This seems to be a promising way to establish a direct assignment of secondary ions to specific functional groups. In this way the quantitative chemical analysis of surface functionalities by TOF-SIMS should become possible without derivatization.

4:00pm **AS-ThA7 Determination of Helical Conformation Effects in PTFE NEXAFS Spectra with FEFF8 Calculations*, D.G. Castner,*** *L. Gamble,* University of Washington*; D.A. Fischer, B. Ravel,* National Institute of Standards and Technology

Near edge X-ray absorption fine structure (NEXAFS) experiments can provide information about the orientation of adsorbed small molecules, self-assembled monolayers and polymers. Long fluorocarbon chains are known to have a twisted (or helical) structure due to the steric interactions of the fluorine atoms. FEFF8 calculations of the C K-edge and F K-edge spectra of poly(tetrafluoroethylene) (PTFE) have been done to determine how changing the helical structure of the PTFE chains affects the NEXAFS spectra. Experimental NEXAFS spectra were obtained at beamline U7A of the NSLS on highly-oriented PTFE samples prepared by rubbing a block of PTFE across a gold-coated silicon wafer heated to 150°C. The helical chains in this well-ordered film are oriented parallel to the gold surface and along the rubbing direction. A large polarization dependence is observed at the F K-edge for the C-F @sigma@* peak and at the C K-edge for the C-F @sigma@* peaks (at 292.6eV and 299eV) and the C-C @sigma@* peak at (296.4eV). FEFF8 NEXAFS spectra calculated with self-consistent spherical muffin-tin potentials, a full multiple-scattering formalism, the structural coordinates for bulk PTFE, and no adjustable physical parameters are in good agreement with the experimental NEXAFS spectra. Variation of the F-C-F bond angle in the calcuated spectra showed that when this angle is commensurate with the helicity of the chains, F atoms from adjacent CF2 groups become aligned in the axial direction. This alignment results in a large change in the NEXAFS spectra. Calculations that varied the radial distance of the carbon atom from the molecular axis showed that a "straight" backbone produces significantly different NEXAFS spectra than a helical backbone. Further calculations show that "stretching" and "compressing" the helical chain can also effect the widths, positions, and intensities of peaks in the NEXAFS spectra.

4:20pm **AS-ThA8 Monitoring the Kinetics of Migration/ Absorption/ Desorption/ and Cross-linking in a Curing Silicone Coating, using the QCM-D Technique***, P. Dahlqvist,* Q-Sense AB, Sweden*; **M. Rodahl,*** Chalmers, Sweden*; P. Bjoorn,* Q-Sense AB, Sweden*; M. Berglin, P. Gatenholm,* Chalmers, Sweden

The Quartz Crystal Microbalance - Dissipation (QCM-D) technique allows real time measurements of properties and processes in nm-um thin polymer and bio-films (M.Rodahl et al., Faraday Discuss. 107, 229 (1997)). Via changes in the resonant frequency, f, small mass changes (ng/cm2) are measured. Via changes in the energy dissipation factor, D, energy losses due to internal and interfacial friction in the polymer film are measured. This makes the technique a versatile tool to, e.g., phase transitions and polymerisation kinetics. In this work we studied the cross-linking kinetics of approximately 0.5 um thick films of silicone (PDMS) in the presence of various concentrations of catalyst and cross-linker (Tridecafluoro - 1,1,2,2, -tetrahydro - octyl triethoxysilane) (FTEOS), at varying humidity. The fluorine-rich FTEOS migrates to the surface due to phase separation and due to minimisation of the systems surface energy. The kinetics of the migration has been monitored and found rapid, most of the migration take place in the first 15 minutes. Water adsorption and ethanol desorption were monitored over time. The water absorption is dominant in the start of the reaction, but after a few minutes to hours, depending on relative humidity, catalyst and FTEOS concentration, the ethanol desorption becomes dominant. The cross-linking rate monitored with the dissipation factor, is highest in the beginning and slowed after 0.5 - 5 hours, depending on relative humidity and catalyst concentration.

4:40pm **AS-ThA9 Angle Resolved XPS Study of Random Fluoro-methacrylate Copolymers***, **W.E. Kosik**, S.H. McKnight, J.M. Deitzel, N.C. Beck Tan,* Army Research Laboratory

Design and control of polymer surface functionality is desirable for numerous applications. It is widely known that hydrophobic polymer surfaces can be produced on block-copolymers due to surface segregation of hydrophobic blocks, including flouro and siloxane species. Less research has been performed on random copolymer compositions. In this work, we investigate the surface segregation of a random copolymer of polymethylmethacrylate (PMMA) and tetrahyrdorperflouroctyl acrylate (PTAN). Copolymers containing different ratios of the two repeat units were examined. Thin films (150-200 nm) were solution spun-cast onto silicon substrates. As-deposited and samples annealed above the copolymer glass transition temperature were studied to assess the degree of surface reorganization that might occur. Angle resolved XPS was used to study the fluorine content of the thin films as a function of depth. It was observed that the concentration of fluoro groups increases near the surface of the film in all compositions. The degree of surface segregation was dependent on the PTAN to PMMA ratio of each copolymer. Furthermore, the segregation was enhanced after annealing of the films at elevated temperatures. Water contact angle measurements were in agreement with the angle resolved XPS results. Potential applications of these materials for selectively permeable membranes are discussed.

5:00pm **AS-ThA10 Surface Analysis Characterization of Titanium/Sol-Gel/Polyimide Adhesive Systems***, **J.T. Cherian,*** Boeing Materials Technology & University of Washington*; D.G. Castner,* University of Washington

Bonded titanium alloys are being evaluated for use at an operating temperature of 175°C. Determining the locus of failure for bonded titanium lap-shear specimens is part of a larger effort to develop durable, environmentally safe surface treatments for titanium alloys. Surface-treated titanium alloy (Ti-6Al-4V, Ti3Al-2.5V, and Ti15V-3Al-3Cr-3Sn) plates are bonded in a standard lap-shear specimen configuration and exposed to temperature for specified intervals. The lap-shear bond joint consists of two etched titanium panels that are coated with a silicon and zirconium containing sol-gel, primed with a polyimide, and then bonded together with adhesive and supporting scrim material. The lap-shear specimens are tested for overall strength and failure modes. Specimens with cohesive failure modes were examined with ESCA and ToF SIMS to determine the composition of the bond joint failure layer. Although the failure was located closer to the sol-gel/polyimide interface than to the Ti/sol-gel interface, ESCA and ToF SIMS analysis revealed that the actual location (sol-gel, primer, etc.) of the failure varies from spot to spot across a given specimen. SEM analysis suggests that the rough surface of the titanium oxide introduces stress at the interface and promotes the non-uniformity of the failure regimes. A model system is being used to investigate the interfacial bonding chemistry between the sol-gel and the polyimide primer. Pure titanium is deposited onto silicon wafers to create a smooth titanium substrate. Smooth, thin layers of sol-gel and polyimide coatings are then spun onto the Ti surface. AFM is used to measure the surface roughness of each layer. ESCA analysis in conjunction with pentafluorobenzaldehyde derivatization is used to follow the changes in the bonding chemistry at the sol-gel/polyimide interface as the sample is cured.

Electronic Materials and Processing Division
Room 608 - Session EM1-ThA

Chemical Mechanical Planarization

Moderator: Y.J. Chabal, Bell Laboratories, Lucent Technologies

2:00pm **EM1-ThA1 Surface Chemical Changes during Cu Chemical Mechanical Polishing***, **S. Seal**, D. Tamboli, V. Desai,* University of Central Florida*; S. Joshi, G. Shinn,* Texas Instruments

The current USLI manufacturing technology is continued to be driven towards miniaturization of integrated circuits (< 0.1 micron feature size). As the devices and circuits have increased their complexity, densification and miniaturization, CMP has emerged to be the key technology for feature sizes of 0.35 micron and below to meet the stringent requirements for next generation microelectronic devices. Cu CMP@footnote 1@ is the "technology" for producing submicron Cu line in multilevel metallization structures and satisfies the global planarization, the most important issue for lithography. During Cu CMP, oxidation, dissolution and surface modification take place due to slurry/wafer interaction. While electrochemical measurements are performed to determine corrosion rate, degree of surface passivation and dissolution, detailed surface chemistry is carried out using XPS and AES techniques. Special emphasis is focused on monitoring changes in copper oxide/hydroxides stoichiometry. The surface chemical changes are correlated to Cu polishing rate and slurry chemistry @FootnoteText@ @footnote 1@J. M. Steigerwald, S. P. Muraraka and R. J. Gutmann, Chemical Mechanical planarization of Microelectronic Materials, John Wiley and Sons, Inc. 1997.

2:20pm **EM1-ThA2 Effect of Thin Film Properties on Copper Removal in CMP***, **D. Tamboli**, S. Seal, V. Desai,* University of Central Florida*; S. Joshi, G. Shinn,* Texas Instruments

Currently there is a significant efforts directed towards integrating copper interconnect technology into semiconductor device fabrication because of advantages such as lower RC delays and superior electromigration performance with the use of copper. CMP of copper is a relatively new technology. It is also extremely challenging because of low hardness of Cu films (which makes it prone to defects such as scratches, dishing etc.) and its poor electrochemical properties. Performance of Cu-CMP process is greatly dependent on properties of the deposited copper films. In this study, we report the effect of thin film properties on CMP performance of Cu. As deposited Cu films are first characterized using techniques such as XPS, glancing angle XRD (to measure internal stress), AFM (to study grain morphology), nano-indentation and 4-probe sheet resistivity measurement, and electrochemical polarization measurements. These wafers are then polished. CMP performance as measured by removal rates and in-situ dissolution rate measurements is then correlated with the thin film properties of Cu.

2:40pm **EM1-ThA3 Damascene Patterning of Advanced Interconnect Structures***, **R.J. Gutmann,*** Rensselaer Polytechnic Institute **INVITED**

Advanced IC interconnect structures incorporate damascene patterning (in-laid metal) to improve packing density and reduce manufacturing cost. Chemical-Mechanical Planarization (CMP) of copper or aluminum is used to delineate the trenches and/or vias after dielectric etching and metal deposition. The Damascene patterning process is presented, with an emphasis on CMP issues. The role of the metallic liner and the interlevel dielectric (ILD) are highlighted, the effect of alternative CMP consumables (slurries and pads) discussed, and the interaction between the CMP process and post-CMP cleaning in establishing a robust manufacturing capability presented. Examples used to highlight these issues will include dual Damascene patterned copper interconnects with polymer ILDs and tantalum liners and single Damascene patterned copper and aluminum interconnects with oxide ILDs and magnetic liners. The possibility of scaled copper interconnects without conventional conducting liners will be presented.

3:20pm **EM1-ThA5 Tungsten CMP Process Post Tungsten Etch Back Process to Improve the Reliability for Sub-Micron Device Technology**, ***A. Sidhwa***, *H. Minssieux, C. Spinner,* STMicroelectronics, Inc.

In this paper we will discuss the importance of the CMP process used on wafers after the Tungsten Etch Back step. The purpose of the CMP step was to polish of the remaining Tungsten residue from the etch back process along with the Ti/TiN (barrier) layer and stop on the PMD layer. In the back end of the process, metal residues have been a killer defect that can cause significant decrease in the wafer yield. Residue remaining on the underlying surface may cause shorting of the conductive film and create defects that can affect planarity of the top film. Residues seen after tungsten etch back were due to incomplete tungsten etch back process in uneven areas. These residues can impact the metallization, patterning, and etch processes by causing broken metal lines or lines with defects. It is a known fact that during the tungsten etch back process; it is difficult to etch tungsten of the uneven surfaces due to under layer effects. Hence, high defects can be obtained after the WEB (tungsten etch back) step. If the CMP is performed to polish the remaining tungsten residue along with the barrier, most of the defects that were observed by the KLA after WEB step can be completely removed. The number of defects can be reduced drastically after CMP process. A considerable yield improvement due to CMP touch up process can be obtained. In this paper we show a short loop wafer yield map with high defects and compared to the KLA map performed after WEB process, the yield loss on the short loop wafer is directly correlated to the defects observed at the center of the wafer. This paper will show the defects before CMP and defects after CMP touch up step. Also it will discuss the impact on the electrical data and the SWEAT electromigration data due to Tungsten CMP touch up process.

4:20pm **EM1-ThA8 Etching and Cleaning of Silicon Wafers using HF Vapor Process in the Monolayer Etching Regime**, *Y.-P. Han,* ***H.H. Sawin,*** Massachusetts Institute of Technology

We have studied the oxide etching mechanisms of a gas phase HF etching process in a condensed (liquid phase) and a non-condensed regime (gas phase). In the condensed regime, the etching rate of oxide is greatly affected by the flow rate of the reactant stream and the total pressure of reactor, which can change the mass transfer rates of both reactants and products. In the non-condensed regime, the oxide can be etched in both multilayer and monolayer adsorption states depending on process conditions. The gas phase mass transfer rate limits the etching rate in the multilayer adsorption regime while surface reactions are the rate limiting step in the monolayer regime. The rate limiting steps for etching have been studied at various conditions by changing the temperature of the reactor, the partial pressure of the reactants and the flow rate. In the monolayer etching regime, the etching kinetics can be described by a Langmuir-Hinshelwood adsorption mechanism with competitive adsorption between HF and water. The monolayer etching regime shows many advantages over other etching regimes. We have observed a smoother etched oxide surface, a low selectivity against TEOS, and uniform etching over entire 4" wafer. The native oxide grown on the silicon wafer is removed within a minute, as confirmed by contact angle measurement and XPS. Additionally, aluminum lines are not etched or corroded in the monolayer regime, which implies this process can be applied to metal layers. Since there is no condensed layer on the wafer and chamber wall, the pumping speed is rapid enough for use in a vacuum cluster tool under a hard vacuum environment. We believe that the monolayer HF vapor etching process is applicable to in situ contact cleaning and in situ polymeric residue removal process on metal layers.

4:40pm **EM1-ThA9 Chlorosilane Treatment of SiO@sub 2@-Covered Si Surfaces for Modification of their Chemical Reactivity in Si CVD**, ***T. Yasuda***, *M. Nishizawa, S. Yamasaki,* Joint Research Center for Atom Technology (JRCAT), Japan

SiO@sub 2@ surfaces are chemically inert against silane molecules. This nature has made SiO@sub 2@ the most preferred mask material for selective CVD of Si, while there are other device processes that require enhanced nucleation of Si on SiO@sub 2@. Thus a technique to control the chemical reactivity of the SiO@sub 2@ surface should be useful in many aspects of device processing. This paper shows that such control is possible by treating the SiO@sub 2@ surface with a proper chlorosilane gas, SiH@sub n@Cl@sub 4-n@. Experiments were carried out using Si(001) wafers covered by an ultrathin SiO@sub 2@ layer formed by plasma or UV-ozone oxidation. Our previous studies showed that this layer acts as a mask in Si CVD using Si@sub 2@H@sub 6@.@footnote 1@ An exposure of the SiO@sub 2@-covered sample to SiCl@sub 4@ at 500 K formed surface-SiCl@sub x@ groups as confirmed by on-line Auger electron spectroscopy. We have found that Si deposition is strongly suppressed on the SiCl@sub 4@-treated SiO@sub 2@ surface under our standard CVD condition (0.05 Pa Si@sub 2@H@sub 6@; 853 K). Density of the Si nuclei is much smaller (~10@super 8@ cm@super -2@) than those observed on the as-oxidized surfaces (~10@super 9@cm@super -2@). This indicates that the surface-SiCl@sub x@ group is inert against Si@sub 2@H@sub 6@. In contrast, Si nucleation is greatly enhanced by a SiH@sub 2@Cl@sub 2@ treatment, the nucleation density reaching 6 x 10@super 10@ cm@super -2@. We have also found that electron-beam irradiation of the chlorosilane-treated surfaces prior to the CVD processing enhances Si nucleation. The minimum electron dose to induce this effect was 10 mC/cm@super 2@. Taking advantage of this effect we have achieved "resistless" selective deposition on the beam-defined parts of the SiO@sub 2@ surface. This study, partly supported by NEDO, was carried out at JRCAT under the joint research agreement between NAIR and ATP. @FootnoteText@ @footnote 1@ T. Yasuda et al., Appl. Phys. Lett. 74, 653 (1999).

5:00pm **EM1-ThA10 The Passivation of Si(100)-2x1 with Alcohols**, ***T. Bitzer***, *A. Lopez,* St. Andrews University, United Kingdom; *N.V. Richardson,* St. Andrews University, United Kingdom, UK

Wet chemical etching is a fundamental process in the production of nano-structures on silicon wafers. It has been found that the addition of alcohols such as iso-propanol to an aqueous KOH etchant moderates the etching process, which improves the surface finish.@footnote 1@ In this study, we simulated the conditions at the silicon wafer/etchant interface inside ultra high vacuum (UHV) by the passivation of the Si(100)-2x1 with alcohols ((CH@sub 3@)@sub n@CH@sub 3-n@OH, n=1,2,3), such as ethanol, iso-propanol and tert-butyl alcohol, and post-exposure to H@sub 2@O. Vibrational spectra, taken with high resolution electron energy loss spectroscopy (HREELS), show that alcohol species chemisorb via a deprotonation of the OH group. The alkoxy species are bonded to the silicon dimer through a Si-O-C linkage. We found that post-exposure to H@sub 2@O does not result in a removal of alkoxy species but rather in an oxidation of the Si-Si bond of the silicon dimer. After prolonged H@sub 2@O exposure, 2x1 diffraction spots are absent in LEED. The findings will be compared with the reactivity of alcohols on hydroxylated Si(100)-2x1.@footnote 2@ @FootnoteText@ @footnote 1@ S. A. Campbell, K. Cooper, L. Dixon, R. Earwaker, S. N. Port and D. J. Schiffrin, J. of Micromech. and Microeng. 5, 209 (1995) @footnote 2@ T. Bitzer, N. V. Richardson and D. J. Schiffrin, Surf. Sci. Lett. 382, L686 (1997).

Electronic Materials and Processing Division
Room 611 - Session EM2-ThA

Silicon Carbide and Dielectrics on Si

Moderator: R.M. Feenstra, Carnegie Mellon University

2:00pm **EM2-ThA1 Silicon Carbide: Material of the 21st Century?**, ***P.G. Soukiassian***, Université de Paris-Sud/Orsay, France **INVITED**

Silicon carbide (SiC) is a refractory material belonging, with diamond and nitrides, to the wide band gap semiconductor class. SiC has a strong technological interest especially in high temperature, high speed, high voltage and high power semiconductor devices and sensors. Furthermore, rather inert chemically, its ability to resist to radiation damages makes SiC very suitable for hostile environments. In addition, SiC has very interesting mechanical properties and is one of the best biocompatible material. These exceptional properties are driving forces into the present fast growing interest in surfaces and interfaces of this advanced material. The surfaces and interfaces of cubic and hexagonal SiC are investigated by atom-resolved variable temperature scanning tunneling microscopy and spectroscopy and photoemission spectroscopies using synchrotron radiation.@footnote 1-3@ Such important issues as the atomic scale self-propagated surface oxidation and SiO2/SiC initial interface formation will be addressed.@footnote 4,5@ In addition, the discovery of highly stable self-organized Si and C atomic lines having fascinating characteristics and their dynamics will also be described.@footnote 6,7@ The Si nanostructure number and spacing could be mediated by annealing time and temperature leading to ordering ranging from a single isolated Si atomic line to large superlattices of "massively parallel" atomic chains.@footnote 6@ One discovers also a sp to sp3 temperature-controlled diamond-like transformation which could potentially be usefull in diamond growth.@footnote 7@ All these characteristics are unprecedented and show a very novel and interesting aspect of SiC in its ability to also be a very suitable material in nanoscience. @FootnoteText@ @footnote 1@F. Semond, P. Soukiassian, A. Mayne, G. Dujardin, L.Douillard and C. Jaussaud, Phys. Rev. Lett. 77, 2013 (1996). @Footnote 2@P. Soukiassian, F. Semond, L. Douillard, A. Mayne, G. Dujardin, L. Pizzagalli and C. Joachim, Phys. Rev. Lett. 78, 907 (1997). @Footnote 3@V.Yu. Aristov, L. Douillard, O. Fauchoux and P. Soukiassian, Phys. Rev. Lett. 79, 3700 (1997). @Footnote 4@A. Mayne, F. Semond, G. Dujardin and P. Soukiassian, Phys. Rev. B 57, Rap. Comm., R 15108 (1998). @Footnote 5@F. Semond, L. Douillard, P. Soukiassian, D. Dunham, F. Amy and S. Rivillon, Appl. Phys. Lett. 68, 2144 (1996). @Footnote 6@P. Soukiassian, F. Semond, A. Mayne and G. Dujardin, Phys. Rev. Lett. 79, 2498 (1997). @footnote 7@V. Derycke, P. Soukiassian, A. Mayne, G. Dujardin and J. Gautier, Phys. Rev. Lett. 81, 5868 (1998).

2:40pm **EM2-ThA3 Characterization of PECVD SiC and its Application in Advanced Reticle Technology-SCALPEL Membrane*, S. Han*,** *W.J. Dauksher, P.J.S. Mangat, K.D. Cummings, S.M. Smith,* Motorola, Inc.

The material which forms thin membrane layer (1000@Ao@) in Scattering with Angular Limitation Projection Electron Beam Lithography (SCALPEL) mask technology should satisfy a handful of rigid requirements such as stress controllability, high mechanical stiffness and good chemical etch resistance for wet processing. We have demonstrated that amorphous PECVD SiC can be an excellent choice of material that satisfies the criteria above. SiC potentially could be a better candidate for the membrane layer than silicon nitride, which is currently recommended. Furthermore, it has the possibility of better membrane yield and improved image placement because the elastic modulus for SiC is almost twice that for silicon nitride. Amorphous SiC films were prepared by PECVD using SiH4 and CH4 chemistries. The as-deposited intrinsic stress can be varied from mid-compressive to weak tensile depending on the deposition conditions. Furthermore, we have shown that the magnitude and sign of the as-deposited stress in the film can be modulated by RTA anneal cycle. Stress level in the films can be modified to our level of interest (about 1e9 dynes/cm2 tensile.) In addition, the etch resistance in KOH etchant, an important criteria, is improved after the post annealing cycle. This is associated with hydrogen evolution during the annealing, which reduces the density of hydrogen bonds with C and Si. Results will include the yield impact of controlling stress on the membrane by deposition conditions or by post annealing. In addition, characterization results of films using FTIR and RBS for hydrogen bonding and atomic ratio, respectively will be included. In summary, this paper addresses comprehensive information on a uniform, low stress PECVD SiC that can be used as a membrane material for SCALPEL mask technology.

3:00pm **EM2-ThA4 Contact Properties of Cerium Ultrathin Film on SiC***, W.J. Lu, D.T. Shi,* ***T. Crenshaw****, A. Burger, W.E. Collins,* Fisk University

Cerium (Ce) is well known as an excellent catalyst for NO@sub x@ conversion in environmental and automobile exhaust gas control. It has a strong adsorption capability for oxygen containing gases. Ce/SiC has a great potential as a chemical sensing materials for NO@sub x@ which can be operated at high temperature. To the best of our knowledge, the electrical contact properties of Ce/SiC on SiC have not been reported. In this work, the morphology and interfacial composition of Ce ultra-thin films on 6H-SiC and 4H-SiC are investigated after thermal annealing using atomic force microscopy and X-ray photoelectron spectroscopy. The Ce ultra-thin films of about 3 nm thickness are deposited by RF sputtering. The samples are annealed at the evaluated temperatures for 30 minutes in air. The Ce ultra-thin film on 6H-SiC and 4H-SiC has a good uniformity as deposited, and there are no significant morphological changes for both samples after annealing. The Ce on SiC contact is a Schottky contact, and the Schottky barrier heights for Ce/6H-SiC and Ce/4H-SiC as deposited are 1.43 eV and 1.77 eV, respectively. The Ce film is oxidized to be a Ce oxide film after thermal annealing in air. The morphology and the interfacial compositions after annealing will be presented. Key Words: SiC, Ce, AFM, XPS, and Schottky barrier height.

3:20pm **EM2-ThA5 A Thermodynamic Analysis of Silicide and Carbide Formation and Stability of W, Co, V, and Zr Thin Films on Single-Crystal SiC***,* ***W.F. Seng****, M.J. Bozack, P.A. Barnes,* Auburn University*; S.A. Catledge, Y.K. Vohra,* University of Alabama at Birmingham

Electronic devices capable of operation at elevated temperatures require understanding of the chemical reactions which occur at the metal-semiconductor interface. Phases predicted from equilibrium thermodynamics are presented in the forms of both Ellingham and Gibbs ternary diagrams to understand the temperature sequence of silicide and carbide formation and stability of the phases formed at the metal-SiC interface. W, Co, V, and Zr were deposited on single-crystal SiC by electron-beam deposition and annealed to temperatures approaching 1000 C. Resulting phases were identified by AES, XPS, and XRD and compared to the phases predicted by thermodynamic analysis. Limitations of the thermodynamic approach are also discussed.

3:40pm **EM2-ThA6 Deposition of Yttrium Oxide by Yttrium Sputter/Thermal Oxidation and Reactive Sputtering for Advanced High k Gate Dielectrics***,* ***J.J. Chambers****, G.N. Parsons,* North Carolina State University

The advent of 50nm MOSFET devices will require an equivalent SiO@sub 2@ thickness (t@sub ox,eq@) of 10Å. Direct tunneling through SiO@sub 2@ becomes problematic below about 15Å. To maintain low tunneling, the gate thickness must be >15Å, which requires an insulator with k>3.9. We form yttrium oxide on Si by: 1) yttrium sputtering followed by thermal oxidation; and 2) reactive sputtering of yttrium. Conditions for the sputter/thermal oxidation process were yttrium sputter in 4.3mTorr Ar at 25°C then ex-situ furnace oxidation in 1 atm N@sub 2@/O@sub 2@ at 900°C. Conditions for reactive sputtering of yttrium were 4.3mTorr, 25-500°C and an Ar/N@sub 2@O flow ratio of 0.5. Infrared absorption peaks from 400-600cm@super -1@ are present in the FTIR transmission spectra of the sputter/thermal oxidation and reactive sputtered films. These peaks are consistent with the 467, 562 and 698cm@super -1@ absorption peaks present in the spectrum of a 99.9% pure Y@sub 2@O@sub 3@ standard. CV and IV electrical measurements have been performed on films from both processes. Leakage current at 2V of 0.1µA/cm@super 2@ has been measured for sputter/thermal oxidation (t@sub ox,eq@=50Å) and reactive sputtered (t@sub ox,eq@=100Å) films. Using optical thickness measured with spectroscopic ellipsometry, effective dielectric constants are approximately 8.0 for films from both processes. Bulk Y@sub 2@O@sub 3@ has k=14-17, which suggests that the films described here have a reduced k in their thin film form, some yttrium silicate formation and/or an underlying SiO@sub 2@ layer. Under some deposition conditions, inert gas annealing increased inversion capacitance in the CV trace, possibly due to interfacial silicide formation. We will discuss the affects of pre-deposition N@sub 2@ and N@sub 2@O plasma surface treatments on the electrical properties of these films. The chemical and structural changes upon annealing will be investigated using XPS, AFM and RHEED.

4:00pm **EM2-ThA7 Bi@sub 4@Ti@sub 3@O@sub 12@ Ferroelectric Thin Films Deposited on Silicon by Pulse Injection Metal-Organic Chemical Vapor Deposition***,* ***S.K. Lee****, H.J. Kim,* Seoul National University, Korea

Bi@sub 4@Ti@sub 3@O@sub 12@ is one of the well-known bismuth-based layered perovskite materials. This compound has attracted much attention because of its characteristic anisotropic property. Especially, the low coercive field along c-axis, about 3.5 kV/cm, has made Bi@sub 4@Ti@sub 3@O@sub 12@ thin film a very promising gate dielectric for a ferroelectric field effect memory device. For this application, ferroelectric thin film has to be fabricated at low temperature in order to keep the abrupt interface with the semiconductor substrate and the composition of the film has to be uniform. By these requirements, metal-organic chemical vapor deposition (MOCVD) was taken as the fabrication method of Bi@sub 4@Ti@sub 3@O@sub 12@ thin film on p-type (100) silicon substrate. Solid Bi(C@sub 6@H@sub 5@)@sub 3@ and liquid Ti(OC@sub 3@H@sub 7@)@sub 4@ were chosen as precursors of bismuth and titanium, respectively, because of their good stability and complete decomposition ability. However, the great difference in formation kinetics of TiO@sub 2@ and Bi@sub 2@O@sub 3@ made it very difficult to control the Bi@sub 4@Ti@sub 3@O@sub 12@ /Si interface and the film composition. In order to overcome this problem, pulse injection method was introduced, in which input precursors were varied periodically during deposition for compensating the lower reactivity of Bi(C@sub 6@H@sub 5@)@sub 3@ with oxygen. By this pulse injection method, abrupt Bi@sub 4@Ti@sub 3@O@sub 12@ /Si interface was attained and the composition of Bi@sub 4@Ti@sub 3@O@sub 12@ thin film was also very uniform. The properties of Bi@sub 4@Ti@sub 3@O@sub 12@ thin films were strongly dependent on the substrate temperature and pulse injection conditions.

4:20pm **EM2-ThA8 Film-Formation Mechanisms and Step Coverage of (Ba,Sr)TiO@sub 3@ Films Grown by MOCVD***,* ***Y. Gao****, T.T. Tran, S. Thevuthasan, M.H. Engelhard,* Pacific Northwest National Laboratory*; P. Alluri,* Motorola, Inc.

Isotopic labeling experiments (@super 18@O@sub 2@) have been carried out to understand the film-formation reactions in the MOCVD growth of (Ba,Sr)TiO@sub 3@ (BST) thin films using Ba(thd)@sub 2@, Sr(thd)@sub

2@, and Ti(O-iPr)@sub 2@(thd)@sub 2@ as the metalorganic precursors. Time-of-flight secondary ion mass spectrometry (TOF-SIMS) 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 phase oxidants (@super 18@O), and the precursor ligands (@super 16@O). The amount of @super 18@O and @super 16@O in these films was also determined by nuclear reaction analysis (NRA). The results are in agreement with the TOF-SIMS data. Thus, the isotopic labeling study reveals two film-formation reactions: oxidation and thermal decomposition of the precursor molecules during the MOCVD growth. The results show that about two thirds of M-O bonds in the original precursors are preserved in the BST films grown at 650 °C in O@sub 2@. However, more precursor molecules are oxidized by O@sub 2@ at 590 °C, indicating that the ligand substitution by O@sub 2@ plays an important role in the film-formation at lower temperatures. Use of a 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 film, indicative direct involvement of N@sub 2@O in the film-formation reactions. Addition of N@sub 2@O in O@sub 2@ also appears to improve film surface morphology and step coverage. The BST films deposited at 650 °C in the 50%O@sub 2@-50%N@sub 2@O mixture exhibit conformal step coverage, excellent crystallinity, and good dielectric properties. The correlation between the film-formation mechanisms, step coverage, crystallinity, and dielectric properties will be discussed in this presentation.

4:40pm **EM2-ThA9 Anhydrous Zirconium (IV) Nitrate as a CVD Precursor for ZrO@sub 2@***, R. Smith, N. Hoelien, C. Taylor, T. Ma, S. Campbell, W.L. Gladfelter,* ***J.T. Roberts,*** University of Minnesota*; M. Copel, D.A. Buchanan,* IBM T.J. Watson Research Center*; M. Gribelyuk,* IBM

We report the chemical vapor deposition (CVD) of ZrO@sub 2@ from the anhydrous metal nitrate, zirconium (IV) nitrate [Zr(NO@sub 3@)@sub 4@]. Zirconia films were deposited onto 100-oriented Si substrates using thermal CVD methods. Measurements of the ZrO@sub 2@ growth kinetics imply an exceedingly low barrier for ZrO@sub 2@ nucleation on a Si(100) surface, as there was essentially no induction period between the onset of CVD and the achievement of steady-state growth. The films were extensively characterized with respect to their suitability as high dielectric constant materials in advanced microelectronic devices. Ion beam methods (Rutherford backscattering, RBS, and medium energy ion scattering spectroscopy, MEIS) suggested that the films were close to the ideal stoichiometry or slightly oxygen-rich. X-Ray diffraction established that most films were monoclinic ZrO@sub 2@. Cross-sectional transmission electron microscopy (TEM) and MEIS measurements showed that the Si-ZrO@sub 2@ interface consists of a 10-15Å thick interlayerof nearly pure SiO@sub 2@. Finally, electrical characterization measurements established low leakage current densitites across the Si-ZrO@sub 2@ interface. This study adds to a growing body of work on the usefulness of volatile, anhydrous metal nitrates as precursors for high electrical quality metal oxide materials.

5:00pm **EM2-ThA10 A New Approach for the Fabrication of Device-Quality Ge/GeO@sub 2@/SiO@sub 2@ Interfaces Using Low Temperature Remote Plasma Processing***,* ***R.S. Johnson,*** *H. Niimi, G. Lucovsky,* North Carolina State University

It has been shown that low temperature (300°C) remote plasma enhanced processing can separately and independently control interface formation and bulk oxide deposition on silicon substrates. Plasma processing is followed by a low thermal budget thermal anneal, e.g., 30 s at 900°C. This process has been used for the formation of the device-quality gate dielectrics in both NMOS and PMOS devices. In the new results reported in this paper, this process has been modified and applied to germanium substrates to determine if it can provide a successful pathway to device-quality Ge-dielectric interfaces. The new process is similar low temperature (300°C) three-step process consisting of (i) an O@sub 2@/He plasma-assisted oxidation of the Ge surface to form a superficial germanium-oxide passivating film, (ii) deposition of a SiO@sub 2@ bulk film by remote plasma-enhanced CVD from SiH@sub 4@ and O@sub 2@, and (iii) a post-oxide deposition anneal for chemical and structural relaxation. We track the initial stages of the plasma-assisted oxidation of the germanium substrate using on-line Auger Electron Spectroscopy (AES). We then discuss why the O@sub 2@ /He plasma oxidation is critical for prevention of "subcutaneous" oxidation of GeO@sub 2@ -Ge interface during the deposition step. As in the case of Si deives, the oxidation step is required for formation of a device quality interface.

Magnetic Interfaces and Nanostructures Technical Group Room 618/619 - Session MI+NS-ThA

Magnetic Imaging

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

2:00pm **MI+NS-ThA1 Cryogenic Magnetic Force Microscopy Instrumentation***,* ***M. Roseman****, P. Grutter,* McGill University, Canada

We describe our cryogenic magnetic force microscope, operating between 4 and 300 Kelvin. The instrument is designed to fit within a 3" diameter bore of an 8 Tesla magnet. Cooling is achieved through the use of He exchange gas, which is pumped out prior to imaging in order to provide a vacuum of better than 10@super -5@ mbar during operation. The instrument uses a fibre optic interferometer to measure cantilever deflections. Through the use of a phase lock loop, this interferometric signal allows for the tracking of the cantilever resonant frequency with a resolution of 0.25 Hz in a 100 Hz measurement bandwidth. Our cantilevers are commercially available, made of single crystal silicon coated with a magnetic film, and routinely exhibit Q-factors of greater than 100,000 at 4 Kelvin. Piezoelectric-based clamping linear positioners, with step sizes of 50 nm (at 77 Kelvin) and capable of operation in high magnetic fields, perform in-situ tip and fibre approaches. As an effective means of vibration isolation, we suspend the microscope from a soft bellows. Comprised of 70 convolutions, the bellows damps out vibrations by more than an order of magnitude, effectively isolating the microscope from the surrounding environment, including pump vibrations and liquid helium boil-off. Particular attention has been paid to optimizing the signal to noise ratio through a systematic study of various noise sources, with the intent of achieving a thermally limited sensitivity.

2:20pm **MI+NS-ThA2 Modified Tips for High Resolution In-plane Magnetic Force Microscopy***,* ***L. Folks,*** IBM Almaden Research Center*; J.N. Chapman,* University of Glasgow, UK*; M.E. Best, P.M. Rice,* IBM Almaden Research Center*; B.D. Terris,* IBM Almaden Research center*; D. Weller,* IBM Almaden Research Center

Commercial batch-fabricated coated MFM tips have been modified to allow high resolution imaging of the in-plane components of stray field above a sample. A hole of diameter ~ 20nm was milled through the magnetic coating layer to the underlying silicon at the apex of each tip with a focussed gallium ion beam. The tips were then magnetized in the direction parallel to the sample plane. The hole at the apex forms a small pole gap and it is the interaction of the stray field from this gap with the sample stray field which produces the MFM signal. Accordingly, the resolution achievable is determined by the diameter of the hole milled at the apex. Note that such a controlled modification of the magnetic tip coating was suggested by Hill.@footnote 1@ High and low density data tracks, with transition spacings ranging from 1 micrometer to 50 nanometers, written in longitudinal granular recording media have been used to demonstrate the utility of the tips. By comparison of experimental results with simple theoretical models it is shown that the tips are strongly sensitive to the in-plane components of stray field. Furthermore, the modified tips exhibit better resolution than the unmodified tips, as may be seen from a side-by-side comparison of data collected from high density written transitions. The modified tips offer an inexpensive route to high resolution imaging of stray fields associated with in-plane domain structures. Hence they are of particular value for high density magnetic recording media investigations since the in-plane component of stray field is closely related to the signal detected by the recording head. @FootnoteText@ @footnote 1@ E. W. Hill, IEEE Trans. Magn. 31, 3355 (1995).

2:40pm **MI+NS-ThA3 Progress Toward Achieving Single-Spin Force Detection***,* ***B.C. Stipe****, D. Rugar, H.J. Mamin, C.S. Yannoni,* IBM Almaden Research Center*; T.D. Stowe, T.W. Kenny,* Stanford University

Magnetic resonance force microscopy was originally proposed@footnote 1@ as a method for imaging individual electron or nuclear spins. This talk will focus on recent progress toward achieving the necessary force sensitivity, tip field gradient, and spin lifetime to detect a single electron spin under real experimental conditions (i.e., with a sharp, submicron-size magnet mounted on an ultrasensitive cantilever within 100 Å of a sample surface). Characterization of the magnetic tip is especially important since the field gradient from the tip determines of the force from the spin. In addition, the spin relaxation rate can increase in the presence of magnetic field fluctuations from the tip. We have characterized the magnetic fluctuations of the tip at the cantilever frequency based on field dependent dissipation measurements on both Co thin film and NdFeB particle tips.

NdFeB tips showed greatly reduced dissipation/fluctuations due, in part, to their high crystalline anisotropy. These tips should generate field gradients greater than 3 G/Å at the target spin, resulting in a force of more than 30 aN. Using custom fabricated single crystal silicon cantilevers at 2.5 K, we have achieved a force resolution of 2.8 aNHz@super -1/2@ far from the sample surface. However, within 500 Å of the sample, tip-surface interactions can significantly increase the force noise and cantilever frequency jitter. The origin of these effects and methods for reducing them will be discussed. This work is supported, in part, by the Office of Naval Research. @FootnoteText@ @footnote 1@ J.A. Sidles, Phys. Rev. Lett. 68, 1124 (1992).

3:00pm **MI+NS-ThA4 Magnetic Imaging by Spin-polarized Scanning Tunneling Microscopy***, **W. Wulfhekel**, J. Kirschner,* MPI fur Mikrostrukturphysik Halle, Germany

A new approach to spin-polarized scanning tunneling microscopy based on the magneto tunnel effect between a ferromagnetic tip and a ferromagnetic sample is demonstrated. By periodically changing the magnetization of the tip in combination with a lock-in technique, topographic and spin-dependent parts of the tunnel current are separated. This allows to simultaneously record the topography and the magnetic structure of the sample. First results are given for polycrystalline Ni and single crystalline Co(0001) surfaces, revealing a high spin contrast of up to 20% of the tunneling current, low data acquisition times of few ms/pixel and a resolution down to 10nm. The magnetic origin of the observed signal is proven rigorously by recording the domain wall motion due to an applied magnetic field during scanning. Potentials and limitations of this new technique are discussed.

3:20pm **MI+NS-ThA5 Spin-Polarized Scanning Tunneling Spectroscopy: Magnetic Domain Imaging and Beyond***, **R. Wiesendanger**, M. Bode, M. Getzlaff,* University of Hamburg, Germany **INVITED**

Spin-polarized vacuum tunneling from ferromagnetic thin film probe tips into exchange-split surface states of rare-earth thin films is demonstrated and applied to magnetic domain imaging with a spatial resolution below 20 nm. The bias dependence of the spin polarization extracted from tunneling spectroscopy data is found to be in surprisingly good agreement with results from spin-resolved (inverse) photoemission indicating that spin-dependent density-of-states effects dominate over matrix element effects. It is also shown that spin-polarized electronic states can yield high tunneling magnetoresistance. On the other hand, surface contamination leads to a strong decrease of the measured spin-polarisation by impurity-assisted scattering which influences strongly the vacuum-TMR effect as well as the contrast in spatially resolved magnetic imaging applications.

4:00pm **MI+NS-ThA7 Scanning-aperture Photo-emission Microscope for Magnetic Imaging***, **G.M. McClelland**, C.T. Rettner,* IBM Almaden Research Center

We have demonstrated a new technique for magnetic imaging that is ultimately capable of spatial resolution better than 5 nm. In our instrument, photoemission is excited by a laser focused to a 10-micron spot. A scanning aperture above the magnetic surface allows only electrons from a small selected region to reach the electron detector. The magnetization in this region is determined from the dependence of photoemission on the circular polarization of the laser. Images of 10-nm-thick Co-Pt multilayer thin films on sapphire have been obtained. From a cesiated film, a high quantum efficiency of 0.002 was observed from 458 nm laser light. Circular dichroism of +/- 2 % is recorded by alternating the circular polarization of the light while scanning. The tip distance above the surface is maintained by advancing the tip until 1-nA tunneling to a positive sample is observed, then withdrawing 15 nm and switching polarity to detect photoemission through the tip. The resolution we observe agrees well with the 35-nm-sized aperture in the gold tip. From the observed noise, we project that there is enough signal to image at 5 nm resolution if a small enough aperture can be fabricated. Recent calculations show that image forces on the electron from the aperture walls act to make the effective aperture even smaller than the physical diameter. The insensitivity of the instrument to varying magnetic fields should make it ideal for time dependent magnetization measurements in an applied field.

4:20pm **MI+NS-ThA8 Magnetic and Chemical Microanalysis Using SEMPA and SAM***, **G. Steierl**, W. Lutzke, H.P. Oepen, J. Kirschner,* Max-Planck-Institut für Mikrostrukturphysik, Germany

Industrial demands led to an enormous interest in micromagnetic analysis tools that can be applied to a wide range of samples including lithographically produced samples with complex chemical compositions. To meet these requirements a new instrument was designed that combines Scanning Auger Microscopy (SAM) and Scanning Electron Microscopy with Polarization Analysis (SEMPA). The core elements are a Schottky thermal field emitter electron gun with coaxial cylindrical mirror analyzer (PHI-SAN 670), a retractable electron-lens system and a spin detector based on Spin Polarized Low Energy Electron Diffraction (SPLEED). The characteristics of these core elements are described and the performance of the entire system is demonstrated by high-resolution chemical and magnetic analysis of Ni@sub 80@Fe@sub 20@- and Co elements. The microstructures of 50nm thickness were produced by using electron beam lithography and lift-off. Oxidized Si(111)-wafers were used as substrate material with an oxide layer thickness ranging from about 10nm (natural oxide layer) to 1200nm (thermally oxidized). It is demonstrated that the electrical insulation of the microstructures due to the oxide-layer does not impede high resolution domain microscopy, if suitable surface preparation techniques are used. Several details of the domain patterns encountered in microstructures of different geometry (squares, rectangles, disks) and of lateral length ranging from 500nm to 10 µm are reported.

4:40pm **MI+NS-ThA9 Low Temperature Magnetic Domain Imaging with Spin Polarized Low Energy Electron Microscopy***, **E.D. Tober**,* NCEM, Lawrence Berkeley National Laboratory*; G. Witte,* Ruhr-Universität Bochum, Germany*; H. Poppa,* NCEM, Lawrence Berkeley National Laboratory

Spin Polarized Low Energy Microscopy (SPLEEM) has for the first time been employed to examine magnetic surfaces below room temperature. With the recent addition of a liquid nitrogen based cooling stage for our instrument, we have the ability to achieve sample temperatures in the range of 110 - 2200 K. SPLEEM has the advantages of high spatial resolution (~10.0 nm) and atomic height resolution combined with image acquisition at near video rates. A full description of the system design as well as its application in exploring the magnetic domain formation in thin films of Co grown in situ on Pt(111) and Au(111) surfaces will be presented.

5:00pm **MI+NS-ThA10 Ballistic Electron Magnetic Microscopy: Imaging Magnetic Domains with Nanometer Resolution***, **W.H. Rippard**[1], R.A. Buhrman,* Cornell University

A new magnetic imaging technique with nanometer resolution, ballistic electron magnetic microscopy (BEMM), is introduced and used to image magnetic structure in copper-cobalt multilayer films. Magnetic domains are clearly observed and are found to give more than 300% contrast in the resulting BEMM images. Domain wall motion is also studied as a function of applied magnetic field. Magnetic contrast is observed on length scales of less than 100 nm and fluctuations of the ballistic transport in the system are observed on scales of less than 10 nm. The magnetic contrast is found to be strongly dependent on magnetic layer thickness while only weakly dependent on the number of layers in the multilayer stack. An energy dependent difference in the electron transport as a function of the relative alignment between the magnetic layers is also reported, revealing the effects of the Co band structure on the ballistic current transport. Strong magnetic contrast is observed at energies as high as 4 eV, demonstrating a large asymmetry in the effective spin-dependent mean free paths in this system. The local nature of the technique also allows the direct imaging of the effects of interfacial dopants on the ballistic transport in the multilayer films. Results from such dusting studies are also presented.

The Science of Micro-Electro-Mechanical Systems Topical Conference
Room 620 - Session MM+VT-ThA

Vacuum MEMS

Moderator: C.C. Wong, Sandia National Laboratories

2:40pm **MM+VT-ThA3 Quadrupole Mass Spectrometry using MEMS***, **S. Taylor**,* University of Liverpool, U.K., UK **INVITED**

Quadrupole Mass Spectrometers (QMS) find a wide range of applications worldwide. The conventional QMS arrangement uses circular metallic rods as the mass filter excited electrically at voltages up to 1kV depending upon the application. If the size and voltages can be reduced then the range of applications for QMS instruments would increase. The application of MEMS technology allows the fabrication of submillimetre versions of such structures. In this paper the development of a miniature QMS is reported in which the conventional rod arrangement has been replaced with a

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[1] **Falicov Student Award Finalist**

microengineered version. The structure is made in silicon with metallised specially drawn glass fibres of length 20-30 mm and diameter 0.5 mm to act as the quadrupole rods. The correct electrode spacing and alignment are achieved through the use of V-shaped grooves etched into the silicon. This is about one order of magnitude smaller than most conventional QMS filters, with the potential for further reduction in size. The MEMS mass filter was mounted onto a commercial ion source, which was in turn attached to a vacuum flange and supplied by an electronic drive circuit modified to run at 6MHz. Mass spectra in the range 0-50 a.m.u were obtained and these were simulated numerically. The results indicate a linear mass scale with 5-10% valley separation between O2/N2 peaks and a best resolution at 10% peak height of around 2 a.m.u at mass 40. Reliable QMS operation was obtained up to pressures in the 1E-4 to 1E-3 mbar range and the highest operating pressure was felt to be a limitation of the ion source, rather than the mass filter.

3:20pm **MM+VT-ThA5 Miniaturizing an Ultra-High Vacuum Orbitron Pump***, **J.Z. Wilcox**, J. Feldman, T. George,* JPL-Caltech*; M. Wilcox, A. Scherer,* Caltech

NASA has identified the development of miniature vacuum pumps as a key future technology need. Miniature pumps will be needed for miniature instrument applications such as mass spectrometers and electron microscopes. Traditional pumps cannot be flown on microspacecraft due to their size, mass, and power requirements. This talk will discuss a novel approach towards the miniaturization of a particular type of high vacuum pump, known as the "Orbitron" pump. The Orbitron pump is an ion-getter pump that does not require magnetic confinement of the ionizing electrons. The purely electrostatic operation, coupled with a novel ring anode design under the development at JPL, enables miniaturization of the orbitron pump to sub-centimeter dimensions, and in addition may allow integration with instruments for in situ planetary exploration such as the Atmospheric Electron X-ray Spectrometer. The pumping action of the Orbitron pump is based on ionization of gas molecules by externally injected electrons which are trapped into stable helical orbits in a cylindrically symmetric electrostatic field around a positively charged anode. The ionized molecules are accelerated to the cathode and embedded in the surrounding collector. However, the conventional linear anode design does not lend itself to miniaturization very well since a minimum length of anode is required to establish stable orbits. The end losses are circumvented in the ring anode design, and in addition the "planar" geometry of the ring orbitron lends itself to miniaturization as well as ease in interfacing with other micro-instruments such as mass spectrometers, electron microprobes and electron microscopes. The goal of our effort has been to verify the feasibility and scalability of the proposed pump design. We will discuss the results of the validation experiments and modeling, impact on scaling to sub-centimeter dimensions, and compare the results with similar results for the linear anode orbitron.

3:40pm **MM+VT-ThA6 Scaling and Microfabricating a Low-Pressure Inductively Coupled Plasma Source***, Y. Yin, **J. Hopwood**,* Northeastern University

Plasmas are commonly used in many large-scale systems. For example, chemical analysis using optical emission spectroscopy relies on gaseous plasmas to electronically excite the sample. Plasmas are also used as sources of radicals and ions for materials modification and for ion propulsion. In this presentation we will describe the miniaturization of plasma sources to dimensions that are compatible with MEMS. One of the most robust methods of generating a plasma is by inductively coupling an rf field to a low-pressure gas. Inductively coupled plasmas (ICPs) can operate for extended periods in reactive gas environments because ICPs are electrodeless. In addition, the geometry of the impressed rf field creates a high density of electrons with relatively low power consumption. A large-scale planar ICP uses a 10 to 30-cm spiral-shaped coil adjacent to a dielectric vacuum window; this geometry is particularly well-suited to microfabrication as the source is scaled down to dimensions the order of 1 mm. The scaling laws associated with miniaturization have been experimentally investigated in terms of optimum frequency of operation and gas pressure. In addition, the effects of scaling the dimensions on plasma properties such as electron temperature and electron density are also measured and modeled. The decreased dimensions of the coil reduces the inductance of the coil and necessitates a higher frequency of operation. Large scale ICPs typically operate at 13.56 MHz, but 5 mm ICPs function most efficiently at 300-400 MHz. Of particular importance is fabricating a coil with a high quality factor (Q) at the operating frequency. The optimum pressure for initiating the plasma is found to scale with the operating frequency such that the electron-neutral collision frequency equals the power supply frequency. Finally, the plasma sheath, or dark space, does not scale with the source dimensions. This appears to set a lower limit on the physical dimensions of the plasma source.

4:00pm **MM+VT-ThA7 Design and Fabrication of an Electromagnetically Driven Microvalve for Micro Total Analysis Systems***, **M. Shoji**, K. Yanagisawa, M. Hirano,* Nippon Telegraph and Telephone Corporation, Japan*; S. Nakano,* NTT Advanced Technologies Corporation, Japan

Microvalves that control fluid flow over a wide flow rate range, and that are compactly assembled, are in great demand for µTAS, such as micro gas chromatographs. This paper reports on design considerations concerning the electromagnetic actuation and the fabrication of a microvalve that operates at a pressure difference of more than 1 x 10@super 5@ Pa with very low leakage. The valve is fabricated using silicon micromachining techniques.@footnote1,2@ The target specifications are a maximum flow rate of 10@super -1@ Pa m@super3@ s@super -1@, a leak rate of 10@super -9@ Pa m@super 3@ s@super -1@, a maximum power consumption of less than 0.1 W at a pressure difference of 10@super 5@ Pa, and a size of 4 x 4 x 2 mm including the actuation unit. The microvalve has a disk-shaped 1-µm-thick cap with a diameter of 100 µm. Actuation of the valve requires a force of more than 1.5 mN perpendicular to the surface of the cap and a stroke of 5-10 µm. To achieve this actuation, ferromagnetic material is deposited (electroplated) onto the cap and an electromagnet (1.3 x 1.5 x 3.2 mm) is set above the cap to generate an attractive force on the ferromagnetic material. The design parameters were determined by three-dimensional numerical analysis that took account of the nonlinear B-H curves of magnetic materials. When the deposited material was Ni with a thickness of 100 µm, and the distance from the Ni to the magnet was 20 µm, a sufficient force was attained if the formed Ni area was several times larger than the cap area. The analysis also showed that using materials with a higher saturation magnetization than Ni would increase the force, thus enabling the valve to work at a higher pressure difference. The effects of such materials will also be reported. @FootnoteText@ @footnote1@K. Yanagisawa, H. Kuwano, and A. Tago, Microsystem Technologies 2, 22 (1995). @footnote2@M. Hirano, K. Yanagisawa, H. Kuwano, and S. Nakano, Proc. IEEE Micro Electro Mechanical Systems, p. 323 (1997).

4:20pm **MM+VT-ThA8 MEMS Micro-Valve for Space Applications***, **I. Chakraborty**, W.C. Tang, D.P. Bame, T.K. Tang,* Jet Propulsion Laboratory

We report on the development of a Micro-Electro-Mechanical (MEMS) valve that is designed to meet the rigorous performance requirements for a variety of space applications, such as micro-propulsion, in-situ chemical analysis of other planets, or micro-fluidics experiments in micro-gravity. These systems often require very small yet reliable silicon valves with extremely low leak rates and long shelf lives. Also, they must survive the perils of space travel, which include unstoppable radiation, monumental shock and vibration forces, extreme variations in temperature. Currently, no commercial MEMS valve meets these requirements. We at JPL have developed a piezoelectric MEMS valve which attempts to address the unique problem of space. We begin with proven configurations which may seem familiar. However, we have implemented some major design innovations which should produce a superior valve. The JPL micro-valve is expected to have an extremely low leak rate, little susceptibility to shock, vibration or radiation, as well as a wide operational temperature range.

4:40pm **MM+VT-ThA9 Compact Fiber-Optic Pressure Sensors Using Microfabricated Sensing Membranes***, **Y.C. Cho**,* NASA Ames Research Center*; T. George, J. Tamayo,* Jet Propulsion Laboratory

Fiber optic sensors are inherently immune to electromagnetic noise, and are very sensitive, light weight, and highly flexible. A prototype optically-detected pressure sensor was successfully designed, assembled and tested. The sensing technique employed was fiber- optic Fabry-Perot interferometry. The sensing head is composed of an optical fiber terminated in a miniature ferrule with a thin, silicon-microfabricated diaphragm mounted on it. The optical fiber is a single mode fiber with a core diameter of 8 microns, with the cleaved end positioned 50 microns from the diaphragm surface. The diaphragm is made up of a 1.5 mm square, 0.2 mm thick silicon nitride membrane whose inner surface is metallized with layers of 30 nm titanium, 30 nm platinum, and 200 nm gold for efficient reflection. The measured differential pressure tolerance of this diaphragm is more than 1 bar, yielding a dynamic range of more than 100 dB. Preliminary tests have demonstrated excellent performance for this sensor. Sensitivity measurements of the sensor were compared with that for a 3 mm diameter B&K microphone and were found to be 2 to 4 dB better than the B&K microphone. This sensitivity is better than any existing fiber optic pressure sensor by at least three orders of magnitude. The frequency response of the fiber-optic microphone was steady and uniform within the 100 to 5,000 Hertz design frequency. The compact size and light weight of these sensors gives them several advantages. For measurement of air flows over flight surfaces, the flow-sensor interaction is smaller, providing more accurate measurements of dynamic pressure. Additionally, their small size could allow these sensors to be placed non-destructively on flight surfaces in contrast to present techniques. The fiber optic microphone also has the added advantage of high temperature tolerance, and a solid state preamplifier as in the case of the condenser microphone is not required.

Topical Conference on Emerging Opportunities and Issues in Nanotubes and Nanoelectronics
Room 6C - Session NT+NS+EM+MS-ThA

Nanotubes: Functionalization and Metrology

Moderator: D. Herr, Semiconductor Research Corporation

2:00pm **NT+NS+EM+MS-ThA1 Opportunities and Challenges for Nanotubes in Future Integrated Circuits*, R.R. Doering,*** Texas Instruments **INVITED**

We speculate about a few potential research opportunities that may be of mutual interest to both the microelectronics and nanotube communities. Perhaps the most evolutionary use of nanotubes in integrated circuits would be in the form of "thin films." Such use would capitalize on "bulk" material properties. For example, a layer of nanotubes (with "best metallic" conductivity) might serve as an interconnect film. Alternatively, an insulating nanotube layer (e.g, "modified" CNTs or other tube chemistries) might be used as a low-K dielectric. Even lower K might be achieved by using high-conductivity CNTs as "self-supporting wires," taking advantage of their inherent mechanical strength to eliminate the need for solid insulating layers. Another type of evolutionary use might involve nanotube structures for passive IC components. For example, the huge volume density of surface area looks appealing for DRAM capacitors. A significant amount of current nanotube research is aimed at active devices, which might ultimately replace today's silicon semiconductor switches. One of the most exciting prospects is the potential for more extensive and effective use of the "third-dimension" in integrated circuits. However, as with today's "planar" IC technology, the benefit/cost of "going 3D" will depend on details of the practical fabrication techniques. For nanotubes, this brings up "formation/place/route" issues. Nanotubes may also play a role in future "atomically perfect manufacturing," which may be needed to scale much below about 50-nm features regardless of the type of device technology employed.

3:00pm **NT+NS+EM+MS-ThA4 Simulations of Plasticity and Kink Catalyzed Functionalization of C and BN Nanotubes*, D. Srivastava,*** NASA Ames Research Center*; M. Menon,* University of Kentucky

Routes to plasticity and kink catalyzed chemistry for functinlaization of C and BN nanotubes are investigated via classical molecular dynamics (MD) and generalized tight-bonding quantum molecular dynamics (QMD) methods. The critical strain for plasticity of BN nanotube is found to be more than that for the similar C nanotube. The structural collapse of nanotubes under compression is explored in which we find that the accumulated strain drives the tube in a plastic deformation in which four-fold coordinated tetrahedral bonds form at the location of the collapse. This lowers the elastic limit of compressed nanotubes to much less than what was predicted earlier with classical MD potential methods alone.@footnote 1@ The critical stress needed for this transition, as computed with QMD method, is in good agreement with experimental values observed for compressed nanotubes in polymer composites and graphite to diamond like transition in a bucky-onion pressure cell. Mechanical kink driven side-wall functionalization of C and BN nanotubes is also explored. We find that mechanical twisting and bending of the tube enhances the binding energy (and lowers the cohesive energy) at kink or edge sites by 1-2 eV as compared to the reactivity of undeformed tubes. Highly localized selective functionalization and etching of sidewalls could thus be possible through kink catalyzed chemical reactivity of nanotubes. A preliminary example of the experimental evidence will be shown.@footnote 2@ @FootnoteText@ @footnote 1@D. Srivastava, M. Menon, and K. Cho, submitted (1999). @footnote 2@D. Srivastava, D. W. Brenner, J. D. Schall, K. D. Ausman, M. F. Yu and R. S. Ruoff, to appear J. Phys. Chem. (1999).

3:20pm **NT+NS+EM+MS-ThA5 Nanoindentation and Nanotribology with Carbon Nanotubes***, B. Ni, A. Garg,* ***S.B. Sinnott,*** University of Kentucky

The mechanisms by which carbon nanotubule (CNT) proximal probe tips deform during the nanometer-scale indentation and scratching of surfaces are explored using classical molecular dynamics simulations. The forces acting on the atoms in the simulations are calculated using a many-body, reactive bond-order potential for hydrocarbons. The results show that single-walled and multiwalled CNT tips indented against hydrogen-terminated diamond and graphene surfaces buckle and slip to relieve the applied stress. However, in the case of reactive surfaces, tip-surface adhesion occurs on contact that ultimately destroys the tubule. Furthermore, while shell-shell interactions have little effect on the deformation mechanisms, the multiwalled tubule is stiffer than comparably sized single-walled tubules. Finally, the way in which the deformation of these tubules changes during scratching of diamond and graphene surfaces will be discussed and the results compared to available experimental data. @FootnoteText@ Supported by NASA Ames Research Center (NAG 2-1121) and NSF MRSEC (DMR-9809686).

3:40pm **NT+NS+EM+MS-ThA6 Quantum Chemistry Study of Carbon Nanotube Fluorination*, R.L. Jaffe,*** NASA Ames Research Center

Quantum chemistry calculations are carried out to characterize the products of fluorination reactions of C@sub 60@, C@sub 70@ and carbon nanotubes. The calculations utilize density functional theory with a widely used hybrid nonlocal functional (B3LYP-DFT). C@sub 60@ is known to readily undergo reaction with molecular fluorine to form C@sub 60@F@sub n@ with n<44. C@sub 60@F@sub 18@ and C@sub 60@F@sub 36@ are the predominate products. C@sub 70@ also is known to undergo similar reaction, but the products have not been completely characterized. Less is known about the possibility of fluorinating nanotubes. However, it has been conjectured that highly fluorinated nanotubes may have attractive chemical and dielectric properties. Fluorination of C@sub 60@ and C@sub 70@ is used to benchmark the calculations for nanotubes. Previous studies have demonstrated that polycyclic aromatic hydrocarbons with an externally constrained curvature are good model molecules for studying the functionalization reactions of single-walled carbon nanotubes. Reaction is likely if the products are energetically stable and any activation energy barriers are small. Initial studies for C@sub 60@ and (10,10) nanotubes have shown that the difluoronated products are quite stable and the fluorination reaction is highly exothermic.

4:00pm **NT+NS+EM+MS-ThA7 Gear-like Rolling Motion of Carbon Nanotubes on HOPG*, M.R. Falvo,*** *J. Steele, A. Buldum,* University of North Carolina, Chapel Hill*; D. Schall,* North Carolina State University*; R.M. Taylor II,* University of North Carolina, Chapel Hill*; D.W. Brenner,* North Carolina State University*; J. Lu, R. Superfine,* University of North Carolina, Chapel Hill

Though much work has been done in recent years in exploring nanometer and atomic scale sliding friction, little experimental or theoretical work has been done on rolling and its relation to sliding at this scale. We will present lateral force microscope investigations of frictional phenomena of multiwall carbon nanotubes (MWCNTs) on highly oriented pyrolytic graphite (HOPG), that include all the rigid body motions: sliding, rotating in-plane, and rolling. Using an advanced manipulation interface for AFMs, the nanoManipulator, we study these friction phenomena through sophisticated manipulation experiments where lateral forces are monitored during manipulations. We have manipulated MWCNTs into a state of atomic registry between the lattice of the tube and underlying substrate. Out of atomic registry the friction is smooth and uniform. As the CNT is rotated in the plane of the substrate, three discrete atomically registered orientations are observed marked by a 3-10 fold increase in the lateral force required to remove them from these orientations. Results of molecular statics calculations for this system show that the potential energy as a function of in-plane rotation angle has three deep minima spaced sixty degrees apart corresponding to atomic lattice registry. When the CNT locks into atomic registry, there is a transition from an in-plane rotational motion to a stick-slip rolling motion. Rather than being perfectly cylindrical, our lateral force data during rolling indicate that the CNT may be faceted (polygonal cross section). MS calculations indicate that faceting is to be expected for MWCNT depending on diameter and wall thickness. The calculated friction expected for rolling a faceted MWCNT agrees well with experimental lateral force data. Molecular dynamics calculations will be shown that lend insight into the energy loss mechanisms for both the sliding and rolling case. This work is supported by the NIH (NCRR), NSF, ONR (MURI), and ARO (DURIP).

4:20pm **NT+NS+EM+MS-ThA8 Selectivity and Diffusion of Binary Fluids in Carbon Nanotubes***, **Z. Mao**, S.B. Sinnott,* University of Kentucky

Carbon nanotube bundles have been proposed as good materials for the manufacture of tailored ultrafiltration membranes due to their uniform, porous structure. In contrast to conventional membranes produced by only partially sintering a ceramic or stretching a polymer, a nanotube membrane would offer the advantages of fewer blocked pores and a narrower distribution of pore sizes. To investigate the properties of a nanotube membrane, the adsorption of simple binary fluids within single tubules and tubule bundles are modeled using atomistic simulations. Specifically, classical molecular dynamics simulations are performed using a combined many-body, reactive bond-order and Lennard-Jones potential. The results show how the diffusion of these molecules proceeds at differing rates within the nanotubes as a function of the diameter and helical structure of the tubules, the density of the fluid, the size difference between the molecules, and temperature. An example of a binary fluid that has been studied is a mixture of CH@sub 4@ and C@sub 4@H@sub 10@ at room temperature. The simulations predict high selectivity in the diffusion of these molecules through the nanotubes. They also allow for the determination of the type of diffusion followed by each type of fluid molecule. Comparisons will be made between these simulation results and the results of similar studies in the literature of diffusion in zeolites and other molecular sieves. @FootnoteText@ Supported by NASA Ames Research Center (NAG 2-1121) and NSF MRSEC (DMR-9809686).

4:40pm **NT+NS+EM+MS-ThA9 Improved Tungsten Disulfide Nanotubes as Tips for Scanning Probe Microscopy***, **A. Rothschild**, G. Frey, M. Homyonfer, M. Rappaport, S.R. Cohen, R. Tenne,* Weizmann Institute of Science, Israel

Synthesis and applications of long and hollow WS@sub 2@ nanotubes are described. Although synthesis of nanotubes from various inorganic compounds have been reported, the high yields of uncontaminated nanotubes reported here represents a significant improvement over past efforts by ourselves and others.@footnote 1@,@footnote 2@ The nanotubes are synthesized in a two-step process the first being the creation of WO@sub 3@ nanoparticles by heating a tungsten filament in the controlled presence of water. The second step, sulfidization, resulted in a 30 times increase in the length of these particles without change in width so that nanotubes up to 10 microns in length and 20-40 nm width were formed. These tubes were attached to scanning force microscope (SFM) tips and used to image deep and sharp features inaccessible by sharp silicon tips. Due to their sandwich S-W-S structure, these nanotubes are probably stiffer than the carbon analogs and hence less prone to instabilities under such rigorous scanning conditions. We propose application of these probes for nanophotolithography, aided by the facile excitation of these compounds by visible and infra-red light. Support by the Israel Ministry of Science, Israel Science Foundation, and Applied Materials-Weizmann Foundation are gratefully acknowledged. A.R. is a recipient of the Lavoisier fellowship (France). @FootnoteText@ @footnote 1@ Y. Feldman, E. Wasserman, D.J. Srolovitz, R. Tenne, Science 267, 222 (1995). @footnote 2@ N.G. Chopra, et al, Science 269, 966 (1995).

Plasma Science and Technology Division
Room 612 - Session PS1-ThA

High Fidelity Pattern Transfer

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

2:00pm **PS1-ThA1 High Fidelity Pattern Transfer***, **K. Kasama**, K. Yoshida, N. Ikezawa, T. Uchiyama,* NEC Corporation, Japan **INVITED**

The design rule of ULSI devices is being shrunk rapidly, now approaching to 150~130nm region. Moreover, the requirement of pattern formation fidelity, such as CD accuracy, overlay accuracy, pattern profile and so on, also becomes very strictly. For example, in the case of gate electrode formation, CD accuracy of less than ±10% is required after dry-etching, i.e., within ±15nm for 150nm devices. However, large CD fluctuation is usually generated in lithography process, and its amount reaches to CD budget. So, very tight CD control is necessary in dry-etching. In this presentation, current status of optical lithography will be introduced. Especially, we will discuss CD fluctuations induced by exposure tool stability, optical proximity effect and device topographic effect. In order to improve pattern fidelity, high NA scan exposure system, optical proximity effect correction mask and anti-reflective layer have been adopted as new lithographic techniques. Next, the resist pattern transfer by plasma process will be discussed, by mainly focusing on gate electrode formation. To suppress pattern density dependence (micro-loading effect) as well as gate oxide thickness reduction, we investigated two step etching process by using high density plasma, TCP. In a main etch step, vertical etched profile is formed under the plasma condition of high etch rate and low micro-loading, and then high selectivity etching to gate oxide is applied as a soft landing step. We have achieved good CD control of less than 10% in the 120~150nm gate formation. Moreover, we will mention about resist pattern shrinkage technique during BARC(bottom anti-reflective coating) plasma etching.

2:40pm **PS1-ThA3 High Volume Self Aligned Contact Etch for SRAM***, **U. Raghuram**, J.E. Nulty,* Cypress Semiconductor

Self-Aligned Contact (SAC) technology is used by Cypress Semiconductor in SRAM cells to form contacts which connect local interconnect and diffusion regions. SAC contacts allow designers to reduce the cell size by reducing the poly pitch. SAC technology is made feasible by the selective etch of the interconnect dielectric such as borophosphosilicate glass to the nitride etch-stop. This paper describes the key parameters for a manufacturable SAC etch, namely, gas chemistry, backside helium cooling, and total gas flow/ pressure. Polymer fill in the contacts provides the required selectivity to the etch-stop layer in SAC etch. The polymer profile is controlled by the sticking coefficient, which is controlled by the wafer temperature. Two common mechamisms for SAC etch are incomplete etch, 'grass', caused by excessive polymer deposition, and loss of selectivity, 'punch through', caused by insufficient polymer protection. Freon-23/ Freon 134a based chemistry provides self limiting nitride etch-stop performance. Uniform and constant wafer temperature is critical for process window in an etch controlled by polymer deposition. Using electrostatic chuck technology resulted in a wider process window with respect to backside helium control. The process runs at relatively higher pressures (50-100 mT) and total flows (70-150 sccm). Addition of argon allows the process to run at a moderate pressure and flow. It also improves the process uniformity. Backside helium setting of 8-12 Torr provides good wafer temperature control. The process was first developed for 0.5 micron design rules. The Cypress SAC process has been transferred to two different medium density plasma etcher platforms. This process has also been extended with minor modifications to etch SAC contacts for at least four SRAM technologies ranging from 0.5 to 0.21 micron design rules.

3:00pm **PS1-ThA4 High Density Plasma Oxide Etching of SAC (Self-Aligned Contact) and 0.25 micron HARC (High Aspect Ratio Contact) Structures: Process and Repeatability Results***, **L. Marquez**, B. Bosch, O. Turmel, S. Darcy, J.M. Cook,* Lam Research

A major challenge of SiO@sub2@ etching for sub-0.25 micron design rules is the stability of the process both long and short term. The very small, often deep, features together with the requirement for high selectivity guarantee that a very high degree of control of both the hardware and the process is essential. Stable SAC and HARC (> 10:1 aspect ratio) processes have been developed in an inductively coupled, high-density plasma dielectric etch tool. The repeatability of the processes was found to be dependent on the stability of the reactor's surface temperature, the material properties of the reactor's walls and the overall cleanliness of the chamber. The trends (etch rate, selectivity, uniformity, etc.) of the processes have been investigated in terms of power, pressure, flow, chemistry and wall temperatures. It is necessary to understand these trends in order to optimize the various process parameters such as selectivity and uniformity. The impact of surface temperature and material properties on the process results will also be discussed. Several marathons with both the SAC and HARC processes have demonstrated the manufacturability of both the processes and the high density plasma dielectric etch tool. The results of these marathons will be presented.

3:20pm **PS1-ThA5 The Angular Dependence of SiO@sub 2@, Si@sub 3@N@sub 4@, and Poly-Silicon Etching Rates in Inductively Coupled Fluorocarbon Plasmas***, **C. Hedlund**,* Uppsala University, Sweden, Usa*; F. Engelmark, H.-O. Blom,* Uppsala University, Sweden*; M. Schaepkens, G.S. Oehrlein,* State University of New York at Albany

Modern plasma etching processes, like self aligned contact (SAC) etching and the damascene and dual damascene dielectric etching, put new demands on the patterning processes. In the fabrication of self-aligned contacts, for instance, the silicon dioxide etching process has to stop on the curved silicon nitride spacer surface. At this curved surface a reduced SiO@sub 2@ to Si@sub 3@N@sub 4@ selectivity commonly is observed. In order to investigate the behavior of the angular dependence of the etch rate and the surface chemistry we prepared structures with a precise angle between the structure surface and the normal of the wafer surface by highly selective wet chemical etching of crystalline silicon. These micro machined structures consisting of either V-grooves or free standing rectangular mesas are ten times smaller than the plasma sheath, resulting in a ion flux normal to the wafer surface. The angular dependence of SiO@sub 2@, Si@sub 3@N@sub 4@, and Poly-Silicon etch rates have been studied in inductively coupled fluorocarbon plasmas. Our data indicate that the reason for the lower selectivity at inclined Si@sub 3@N@sub 4@ and poly-silicon surfaces is the angular dependence of the fluorocarbon film deposition and etching rates. At selective SiO@sub 2@ to Si@sub 3@N@sub 4@ conditions a relatively thin fluorocarbon film is formed on curved surfaces and corners as compared to planar surfaces. The surface chemistry and film thicknesses have been investigated with spectroscopic ellipsometry and. X-ray electron spetroscopy (XPS). The results will be presented along with SEM micrographs of etched structures.

3:40pm **PS1-ThA6 Process Optimization of Plasma Polymerized Resists for Advanced Lithography Applications***, **O. Joubert**,* CNET/CNRS, France*; C. Monget,* CNET France Telecom, France*; L. Vallier,* CNET France Telecom*; T.W. Weidman,* Applied Materials

CVD photoresist processes based on the plasma polymerisation of organosilane precursors such as methylsilane or dimethylsilane are currently investigated as a technique to extend 248 and 193 nm lithography. Upon exposure to UV light in air, these materials are oxidized generating areas which become more etch resistant to halogen based plasma than unexposed areas, providing a versatile approch to negative tone processes. Films have been deposited in a DXZ chamber from Applied Materials dedicated to dielectric deposition. Exposures have been performed using 248 nm (ASML /300) and 193 nm steppers (ASML /900 and Exitech microstepper). Film development was performed in high density plasma sources using mixtures of Cl@sub 2@, HBr and O@sub 2@. In all cases, developed CVD resist images are transferred through 500 nm of hard baked organic resist using SO@sub 2@/O@sub 2@ gas mixtures. This work reports the lithographic performance at 248 and 193 nm obtained with these dry resists (resolution down to 0.18 µm L/S at 248 nm and 0.13 µm L/S at 193 nm is achieved). Photosensitivity of the films, which can be tuned using the deposition parameters is strongly correlated to the film structure and density. In particular, FTIR analyses show that the photosensitivity increases with the methyl groups content, which favors an increase of the oxygen permeability in the film. The plasma development step is the most critical step of the process since the most serious issues in the dry lithographic process to achieve a good CD control across the wafer. Etch process parameters such as selectivity and uniformity are the more relevant parameters to control the final line width and profile before transfer into the underlaying organic layer. The performance and limitations of the all dry CVD process will be presented. @FootnoteText@ @footnote 1@ This work has been carried out within the GRESSI Consortium between CEA-LETI and France Telecom-CNET

4:00pm **PS1-ThA7 DUV Resist Degradation and Surface Roughening under Plasma Exposure***, **W.H. Yan**,* Microelectronic Division, IBM Corp.*; W. Moreau, R. Wise, Y. Cui,* IBM Corp.

This study investigate the plasma etch characteristic of several different types of DUV photoresist. It has been established that these photoresists suffer from degradation under exposure to common etch processes. We have demonstrated that resist degradation and surface roughening depend on resist polymer composition and etching process conditions. Results from this study clearly indicated: (1) Acrylate component in the polymer breakdown via chain scission during etching. That polymer breakdown causes resist surface pitting. (2) Ion bombardments, etch gas radicals, atoms and polymer deposition from etching reaction in the etching chamber further roughen the resist surface. (3) Heat and UV light in the etching chamber, on the other hand, crosslink resist polymer. The degree of crosslinking highly depends on resist polymer composition. We also investigated UV hardening, E-beam treatment as well as their impacts on resist etch resistance and surface roughening. Results showed that these treatments improve resist etch resistance, but not surface roughness. SEM and AFM were used to study resist surface and sidewall roughness. Gel Permeation Chromatography (GPC) was employed to analyze resist reaction under plasma exposure. The mechanism of resist roughness and its dependence on resist composition was discussed.

4:20pm **PS1-ThA8 Transfer Etching of Bilayer Resists in Oxygen-based Plasmas***, **A.P. Mahorowala**, K. Babich, Q. Lin, D.R. Medeiros, K. Petrillo, J. Simons, M. Angelopoulos,* IBM T.J. Watson Research Center*; G.W. Reynolds, J.W. Taylor,* University of Wisconsin, Madison

Thin film imaging offers the possibility of extending 248 nm lithography to sub-150 nm resolution. We have been working on a 248 nm bilayer resist scheme which utilizes a thin Si-containing resist on top of a thick, planarizing underlayer. The image is developed in the top layer and then transferred to the underlayer via an oxygen-based plasma etch. This paper will focus on two aspects of the critical transfer etch step - 1) etch resistance of the imaging resist and 2) control of profiles and resist roughening. The imaging resist thickness loss rate during the transfer etch is characterized by a rapid decrease in the first 10 seconds followed by a slow rate for the remaining etch. The relative importance of three phenomena occurring when Si-containing resists are exposed to oxygen-based plasmas - 1) oxidation of silicon, 2) deprotection of resist moieties, and 3) plasma etching of resist, will be discussed. FTIR studies on resist films indicate minimal film deprotection-related losses. XPS spectra show that the extent of surface oxidation increases initially and then becomes constant. Thus, this category of resists follows the model proposed by Watanabe and Ohnishi describing the etching of Si-containing resists as a combination of the oxidation of the silicon species and sputtering of the oxide-type layer formed. Post-transfer etch profiles using an oxygen plasma will be shown, and methods to reduce imaging layer resist faceting and thickness loss either by modifying the imaging layer silicon content or shifting to plasma chemistries causing sidewall passivation will be discussed. The effect of different etching chemistries and conditions on imaging layer roughening and striation formation on underlayer sidewalls will be explained with the aid of SEM micrographs and AFM images of etched feature sidewalls. The printing of 125 nm line/space patterns, and 150 nm trench features with 10:1 aspect ratios, in the underlayer will be demonstrated.

4:40pm **PS1-ThA9 Integration of Metal Masking and Etching for Deep Submicron Patterning***, **C.T. Gabriel**, R. Kim, D.C. Baker,* VLSI Technology

Although copper damascene interconnects offer many advantages over conventional subtractive etched Al alloys, the challenges and costs associated with converting to copper have combined to extend the useful life of Al alloy etching into the deep submicron regime. As a result, metal masking and etching are facing new challenges. DUV photolithography has replaced the conventional i-line technique for patterning fine metal pitches, but some DUV photoresists are less able to withstand the aggressive plasma environment than their i-line counterparts. Reflectivity increases at DUV wavelengths, so dielectric anti-reflective films are added on top of the metal stack. The mask-open process, where the dielectric film is plasma etched prior to etching the metal stack, alters the photoresist further and influences the subsequent metal etch. Aspect ratio dependent etch effects increase when etching narrow spaces resulting from tightened metal pitches, and gas additives may be required to protect the metal sidewalls. These effects are characterized and the challenges of deep submicron metal etch process development are discussed. The option of true hardmasked etching of the metal stack is also investigated.

5:00pm **PS1-ThA10 Manufacturable Aluminum RIE Processes for 150 nm and Beyond***, **G. Stojakovic**, X.J. Ning,* Siemens Microelectronics Inc. at IBM/Siemens/Toshiba DRAM Development Alliance*; E.W. Kiewra,* IBM Microelectronics at IBM/Siemens/Toshiba DRAM Development Alliance*; W. Kocon,* IBM Microelectronics

Three different aluminum etch processes - all proven to be manufacturable - have been developed for 150nm line/150space structures. The three schemes are: Organic ARC with photoresist as an etch mask, inorganic silicon oxynitride dielectric ARC (DARC) with photoresist as an etch mask, and a tungsten cap layer as a hard mask. The total metal stack height used in this work was 435 nm, with top and bottom Ti/TiN diffusion barriers. The designed aspect ratio of the wire for a 175 nm technology is 2.5, with a worst case of approximately 3.2. For 150 nm lines, this aspect ratio is substantially higher. For the two processes that use photo resist as the etch mask, the main task of the RIE process is to minimize the consumption of the resist during etch (i.e. maximize the etch selectivity of metal to resist). The metal etch tool used in this work was a commercially available plasma reactive ion etch system. The etch sequence starts with an ARC, DARC, or W hard mask open, followed by a Cl2/BCl3 based Al stack etch. An overetch is performed after a triggered end-point. Subsequent processing includes a down-stream H2O/oxygen plasma ash, followed by a water rinse. The key process parameters, such as gas flow rate, flow ratio of gases, and temperature that affect the metal profile and yield are discussed. It is shown that the RIE process can clear a sub-100 nm space for metal stacks having a height of over 400 nm. This indicates that aluminum RIE can be extended for even smaller structures. In the schemes that use photoresist as etch mask, the thickness of total metal stack is limited by the thickness of the photoresist. In the scheme that uses a PVD W hard mask, the total metal thickness is not a limiting factor for metal etch. The electrostatic chuck temperature plays a major role influencing metal profile and shorts yield.

Plasma Science and Technology Division
Room 609 - Session PS2-ThA

Pulsed Plasmas

Moderator: V.M. Donnelly, Bell Laboratories, Lucent Technologies

2:00pm **PS2-ThA1 Power Modulated, Inductively-Coupled Plasmas***, **M.V. Malyshev**, V.M. Donnelly, J.I. Colonell, K.H.A. Bogart,* Bell Laboratories, Lucent Technologies*; S. Samukawa,* NEC Corporation, Japan **INVITED**

A review of plasma behavior in a power modulated (pulsed plasma) mode will be presented. Time dependencies of electron, positive ion, and negative ion densities as well as electron temperatures and electron energy distribution functions were measured with Langmuir probe, microwave interferometry, and TRG-OES in chlorine containing plasmas. Transition from an electropositive plasma to an ion-ion plasma in the afterglow of the pulsing period will be discussed. Formation of an ion-ion plasma is observed in higher pressure/lower power plasmas where Cl@sub 2@ is dissociated to a lesser degree and significant deinsities of negative ions can be produced through dissociative attachment of Cl@sub 2@. Anisotropic etching in inductively-coupled plasmas requires the use of bias and the effect of rf bias on the pulsed plasma mode of operation will be reviewed. In particular, the transition of the decaying plasma in the late afterglow into an RIE-type plasma during pulsed source and continuous bias operation will be shown and discussed. In this regime of operation, electron temperature sharply decreases in the beginning of the OFF cycle, goes through the minimum, and increases when the capacitive sheath near the wafer starts to heat electrons once the plasma density has decayed to RIE levels. Pulsed-power operation expands the boundaries of traditional plasma processing, and is a promising candidate for reducing plasma-induced damage and profile anomalies during plasma etching. Metal etching results in Lam 9600 TCP reactor show an 80% decrease of the severity of the device damage at an optimum condition of 50 µs ON and 50 µs OFF as compared to that of a continuous wave plasma. The use of power modulation for studying fundamental plasma dynamics will also be discussed.

2:40pm **PS2-ThA3 Method for Ion Energy and Ion Energy Distribution Functions Control at the Substrate during Plasma Processing***, **S.-B. Wang**[1], A.E. Wendt,* University of Wisconsin, Madison

A new method is proposed for control of ion energy and ion energy distribution functions (IEDF) at the substrate during plasma processing. In contrast to the conventional approach of applying a sinusoidal voltage of variable amplitude and frequency to the substrate electrode, the new technique has a variety of advantages and provides a much greater degree of energy control by instead using a specially tailored waveform consisting of a periodic pulse or short high frequency burst in combination with a slow ramp. This rather adaptable technique for controlling the ion energy distribution function has important implications for selectivity and feature profile control in plasma etching, as well as film quality in plasma enhanced chemical vapor deposition (PECVD). In addition, it can be used to non-invasively measure the ion energy flux bombarding the substrate, and, therefore, can serve as a real-time indicator for etching process control and a real-time monitor for the drifting of plasma conditions during plasma processing. A time-dependent spherical-shell plasma fluid model is used to simulate different bias voltage waveforms and different area ratios for powered and grounded electrodes, and thus demonstrate the mechanisms of this method in producing a narrow IEDF of precisely controlled energy, independent of ion mass. Experiments in a helicon plasma using this method of substrate bias confirm predictions of sheath voltage evolution. Taking plasma noise into consideration, an IEDF with a single peak and full width at half maximum of 8 eV is expected for a 20 mTorr argon plasma, independent of the value of DC self-bias.

3:00pm **PS2-ThA4 Modulation Frequency Effects on Metal Etching Processes Using Pulsed-Power Plasma of Cl@sub 2@/BCl@sub 3@ Admixture***, **C.J. Choi**, O.S. Kwon, Y.S. Seol, I.H. Choi,* Hyundai Electronics Industries Co., Ltd., Korea

Using a langmuir probe and mass spectrometry, characteristics of pulsed-power plasmas of Cl@sub 2@/BCl@sub 3@ admixtures have been investigated for Al and TiN etching. From the measurements of ion energy distributions, kinetics of positive and negative ions were studied as a function of modulation frequency. Time-modulation was carried out in the range of modulation frequency from 1 kHz to 500 kHz for a 13.56 MHz radio frequency source. As the modulation frequency decreases, densities of the positive ions such as Cl@sub 2@@super +@ and BCl@sub 2@@super +@ and neutrals were not changed significantly. However, the negative ions of Cl@super -@ and Cl@sub 2@@super -@ increase greatly due to enhancement of electron attachment reactions since high-energy electrons larger than 5 eV were cooled effectively at low modulation frequencies, especially lower than 50 kHz. Etching characteristics for the metal films were also investigated as a function of modulation frequency. Etch rates of both Al and TiN films increased with decrease of the modulation frequency in the range of 1 kHz to 100 kHz. In particular, the Al etch rate at the lowest modulation frequency, 1 kHz, dominates over that in the continuous wave plasma at a fixed average power mode. By correlating the etching characteristics with the results from the plasma diagnostics, we determined the role of negative ions, generated predominantly during the plasma-off period, in metal etching with the pulsed-power plasma. Finally, the plasma charge-up on ferroelectric capacitor was examined after the metal etching with the pulsed-power plasma.

3:20pm **PS2-ThA5 Characterization of Process-Induced Charging Damage in Scaled-Down Devices and Reliability Improvement using Time-Modulated Plasma***, **K. Noguchi**, S. Samukawa, H. Ohtake, T. Mukai,* NEC Corporation, Japan **INVITED**

The charging damage from metal etching and dielectric etching was studied using MOS devices with gate oxide thickness of 1.9-6.0nm, and the impact of the plasma charging on reliability of scaled-down devices, as well as damage monitor methods appropriate for each plasma process and oxide thickness were investigated. Obtained results are as follows. For metal etching, in which electron shading effect is a major cause of charging, hot carrier effect dominated device degradation for oxide of 3.5-6.0nm. For thinner oxide (< 3.0nm), however, a gate leakage failure dominated but the failure rate decreased with gate oxide thinning below 3.0nm and became negligibly small below 2.2nm. For dielectric etching, the gate leakage current was an effective damage monitor, though high oxide electric field of >10 MV/cm was required to detect the latent damage effectively. Charge-to-breakdown or hot carrier degradation was less sensitive to the dielectric etching damage. Similar to the metal etching, the failure rate was lower for thinner oxide. Although the oxide damage seemed to decrease with device scaling, the problem may remain as latent damage or reduced reliability. To realize plasma process with low damage, time-modulated (TM) plasma technology was applied to the ECR metal etcher, the ultrahigh frequency (UHF) dielectric etcher, and the ICP polysilicon etcher. These etchers all showed reduction in charging damage compared to the conventional continuous-wave plasma. For example, the estimated amount of the charging current from the plasma was reduced to 1/4 in the metal etcher. The oxide yield improved by about 2 times in the dielectric etcher. The density of oxide traps created by the plasma process decreased in the polysilicon etcher. Thus, the use of the TM plasma is an effective and practical method to realize scaled-down MOS devices with better yield and reliability.

4:00pm **PS2-ThA7 Reduction and/or Elimination of Undesirable Topographic Differential Charging Effects in Semiconductor Processing by using Simultaneous Modulation of Source and Wafer RF***, **N. Hershkowitz**,* University of Wisconsin, Madison*; M.K. Harper,* Intel Corporation*; B.-W. Koo,* University of Wisconsin, Madison

High aspect ratio features are predicted to exhibit a variety of undesirable effects associated with electron shadowing and the resulting differential charging of dielectrics in semiconductor etching and deposition. Examples include notching in line and space structures, aspect ratio dependent etching, sidewall bowing, microtrenching and charging damage. In agreement with previous work, our experiments with Cl2 plasma etching of poly-Si and C2H2F4 of SiO2 (in a helicon etch tool) have found that modulation of the 13.56 MHz RF source can eliminate topographic charging effects in the absence of RF wafer bias, but fails in the presence of CW RF wafer bias. Data are presented showing that simultaneous source and

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

wafer (on-off) modulation eliminates topograhic-charging effects while preserving the advantages of bias voltage. RF frequency and modulation duty cycle effects are discussed together with discharge mechanisms.

4:20pm **PS2-ThA8 Time-Resolved Optical Measurements of a Pulsed Inductively Coupled Plasma***, **E.C. Benck**, M. Edamura,* National Institute of Standards and Technology

Pulsed high density plasma sources have been suggested as an additional technique to alter plasma properties to help improve plasma etching. Time-resolved diode laser absorption spectroscopy has been used to measure the argon metastable densities in pulsed inductively coupled plasmas. These measurements were made in an inductively coupled version of the Gaseous Electronics Conference rf reference cell with Ar, Ar/O@sub 2@ and Ar/CF@sub 4@ discharges. These results are compared with time-resolved optical emission measurements from excited states of Ar, O and F atoms as well with time-resolved Langmuir probe measurements. Particular emphasis will be placed on the plasma behavior immediately after the turn on of the rf power to the coil and during the capacitive to inductive mode transition.

4:40pm **PS2-ThA9 Substrate and Plasma Heating within High Frequency Bi-polar Pulsed-DC Magnetron Sputtering Applications***, **L.J. Mahoney**, G.W. McDonough, D.C. Carter, G.A. Roche, H.V. Walde,* Advanced Energy Industries

Bipolar pulsed-DC power supplies have been developed and widely used for magnetron sputtering applications where periodic reversal of the sputter target polarity is used to suppress arc events. Pulsed-DC sputter deposition is particularly advantageous with reactive sputter deposition of oxides and select nitrides where arcs can lead to defects in deposited films and coatings. Recent technical advances now allow workers to widely adjust pulsed-DC operation by varying the pulse frequency up to 350 kHz and by varying the pulse-width or duty cycle. We have observed that at frequencies substantially greater than 100 kHz, the rate of change in substrate temperature substantially increases, a condition that can influence deposition processes. To better understand the mechanisms driving the increase in substrate heating, we examine the downstream sputter-deposition region of a closed-field magnetron with six inch diameter Al target by means of (1) fast-response thermal probes to measure the intrinsic power flux to grounded and floating substrates, (2) a time-resolved Langmuir probe to elucidate electron heating dynamics, and (3) analysis of the unique magnetron current and voltage waveforms. At pulsed-DC frequencies above 100 kHz, we observe that the intrinsic power flux density and electron density at the substrate both increase over DC and near DC sputter conditions. The measurements also indicate that the heating effect may be controlled by varying the pulsed-DC frequency and duty cycle. Moreover the heating effect correlates with transient features in the pulse-DC voltage waveform. From this work we infer that the mechanism for heating is likely to be driven by stochastic heating of the plasma electrons through a spatially-varying and time-dynamic sheath at the target, as analogous to conventional AC plasma sources. Potential process benefits of pulsed-DC operation at such high frequencies are also discussed.

Surface Science Division
Room 606 - Session SS1+EM+NS-ThA
Metal/Metal Growth

Moderator: R.Q. Hwang, Sandia National Laboratories

2:00pm **SS1+EM+NS-ThA1 Dislocation Structures of Submonolayer Films near the Commensurate-Incommensurate Phase Transition: Ag on Pt(111)***, **J.C. Hamilton**, R. Stumpf,* Sandia National Laboratories*; K. Bromann, M. Giovannini, K. Kern, H. Brune,* EPF Lausaane, Switzerland

We provide a theoretical explanation@footnote 1@ for unusual experimental observations@footnote 2@ of submonolayer Ag film growth on Pt(111). These films exhibit parallel partial dislocations with narrow hcp regions separated by much wider fcc domains. Using a 2D Frenkel-Kontorova (FK) model we show that this unusually large difference is primarily due to proximity to the commensurate-incommensurate phase transition, and only secondarily to stacking fault energies. We next consider the relationship between island energy, island dislocation structure, and island shape. Using the FK model we calculate the stability of islands with no dislocations, a single dislocation pair across the island, two parallel dislocation pairs across the island, and a "Y" shaped dislocation structure. The model is in excellent agreement with experiment in predicting the onset of dislocation structures in growing islands. It also suggests that the dislocations have little or no effect on the equilibrium island shape. Finally we discuss the relationship between these calculations and related experiments@footnote 3@ on the structure of the clean Pt(111) surface which reconstructs above 65% of the melting point. @FootnoteText@ @footnote 1@ J. C. Hamilton, R. Stumpf, Karsten Bromann, Marcella Giovannini, Klaus Kern and Harald Brune, Phys. Rev. Lett., in press@footnote 2@ Karsten Bromann, Harald Brune, Marcella Giovannini, and Klaus Kern, Surf. Sci. V388, L1107 (1997). @footnote 3@ A. R. Sandy, S.G.J. Mochrie, D.M. Zehner, G. Grubel, K.G. Huang and Doon Gibbs, Phys. Rev. Lett. 68, 2192 (1992).

2:20pm **SS1+EM+NS-ThA2 Non Capillarity Driven Grain Growth in a Strained Cu Ultrathin Film***, **A.K. Schmid**, T. Giessel, N.C. Bartelt, J. de la Figuera, R.Q. Hwang,* Sandia National Laboratories

Properties of metal films are crucially influenced by details of their grain structure. To determine basic mechanisms of grain evolution we have investigated a prototypical granular thin film using LEEM and STM. In two monolayer thick films of Cu on Ru(0001) a uniaxial relaxation relieves the misfit strain (5.5%) with the substrate, leading to a two-dimensional grain structure consisting of three orientationally different domain types. We observed in-situ grain growth using LEEM in dark field imaging mode and took STM snap shots at several stages of the grain evolution. While on large scale of both time and area the total length of grain boundary decreases in order to reduce the free energy of the system an increase of boundary length has been observed locally and on smaller time scale. The observed behavior can not be described within the framework of a Q-state Potts model which has been widely used for the description of grain growth. We show that the long-ranged lateral interactions between the surface atoms in the strained Cu film which are not considered in Potts model are responsible for the observed behavior.

2:40pm **SS1+EM+NS-ThA3 Exchange Processes in Metal on Metal Growth Studied with High-resolution STM***, **M. Schmid**,* Technische Universitaet Wien, Austria **INVITED**

In the early 1990's, after the first atomic-scale studies by field ion microscopy and related simulation calculations it became apparent that many processes in growth of thin films involve exchange of substrate and deposited atoms. It was concluded that interlayer diffusion at steps, the key process determining the growth mode, often occurs by replacing a substrate atom with a deposited atom, pushing the substrate atom onto the lower terrace. A new way to study such phenomena is scanning tunneling microscopy (STM) with atomic resolution and chemical contrast@footnote 1@. We have deposited a small amount of Co on a Pt(111) surface with a high density of steps. In the resulting structure, we can distinguish between substrate (Pt) and deposited material (Co) on an atom-by-atom basis. An analysis of the STM data shows that Co atoms do not descend Pt steps by diffusing over the step, but descend from the upper terrace to the lower by an exchange diffusion process at the step edge with the Pt atoms. The Co atoms descend a Pt step edge by this process neither at straight A nor at B steps, but rather at the corners or kinks of the vacancy islands. These results are in qualitative agreement with simulations based on embedded atom method (EAM) potentials. Other examples of exchange processes can lead to subsurface growth of the deposited material, with substrate atoms floating on top of it. Such phenomena were observed to occur already at or near room temperature when Co was deposited on the Pt(111) and Pt(110) surfaces. @FootnoteText@ @footnote 1@ E. Lundgren, B. Stanka, G. Leonardelli, M. Schmid, and P. Varga, Phys. Rev. Lett., accepted.

3:20pm **SS1+EM+NS-ThA5 Self-diffusion on Pt(110)-1x2: Ab-initio Barriers vs. Experiment@footnote 1@***, **P.J. Feibelman**,* Sandia National Laboratories

Because it requires breaking more bonds, dimer diffusion by dissociation and recombination on clean Pt(110)-1x2 should cost more energy than the recently discovered@footnote 2@ "leapfrog" mechanism. Since cohesion per bond decreases with increasing coordination, the leapfrog mode should also have a lower barrier than monomer diffusion. Though first-principles calculations confirm these deductions, they are at odds with experiment, possibly signalling the influence of low-level surface contamination. @FootnoteText@ @footnote 1@ Work supported by the U. S. Department of Energy under Contract No. DE-AC04-94AL85000. Sandia is a multi-program laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy @footnote 2@ T.R. Linderoth, et al., Phys. Rev. Lett. 82, 1494(1999); F. Montalenti and R. Ferrando, Phys. Rev. Lett. 82, 1498(1999).

3:40pm **SS1+EM+NS-ThA6 Novel Temperature Dependence of the Morphology of Deposited Multilayer Ag/Ag(100) Films*, C.R. Stoldt,*** *A.R. Layson, C.J. Jenks,* Iowa State University*; M.C. Bartelt,* Sandia National Laboratories*; K. Caspersen, J.W. Evans, P.A. Thiel,* Iowa State University

Metal(100) homoepitaxy provides a natural testing ground for recently developed ideas on kinetic roughening and "mound formation" due to step-edge barriers. Non-monotonic variation of roughness with deposition temperature (T) has been predicted,@footnote 1@ but not observed. Here, we report comprehensive VT-STM studies for growth of Ag/Ag(100) films between 130K and 300K which reveal this behavior. Roughness of 25ML Ag/Ag(100) films at first increases "classically" below 300K due to inhibited downward transport, but then decreases below 220K, achieving a low plateau value below 170K. Unlike Pt/Pt(111) and Rh/Rh(111) growth, non-monotonic behavior is not associated with a dramatic change in 2D island morphology, but rather with enhanced downward funneling from (the more prevalent) step edges at lower T. We also characterize the mound morphology, noting the steepness of the mound sides and small lateral dimension at lower T. A breakdown of kinematic scattering behavior of the intensities observed in our HRLEED studies of these films is attributed to this feature. Monte Carlo simulations of a realistic model for growth@footnote 1@ are consistent with and elucidate observed behavior. @FootnoteText@ @footnote 1@M.C. Bartelt and J.W. Evans, Surf. Sci. 423 (98) 189; Phys. Rev. Lett. 75 (95) 4250.

4:00pm **SS1+EM+NS-ThA7 Edge Diffusion During Growth: Kink Ehrlich-Schwoebel Effect and Resulting Instabilities@footnote 1@***, O. Pierre-Louis,* Univ. J. Fourier (CNRS), France*;* ***T.L. Einstein,*** University of Maryland

In addition to the usual step Ehrlich-Schwoebel effect (SESE) on typical metal and semiconductor surfaces, there can also be a kink Ehrlich-Schwoebel effect (KESE), associated with asymmetries in barriers at kinks/corners encountered by atoms during transport along step edges.@footnote 2@ We take into account both phenomena to study the evolution of arbitrarily oriented surfaces during molecular beam epitaxy. We find that the heretofore rarely discussed@footnote 3@ KESE has a profound effect on growth morphology. Under the usual growth conditions, KESE induces a new instability of vicinal surfaces, supplanting the familiar Bales-Zangwill instability@footnote 4@ due exclusively to SESE. The possibility of stable kink flow growth is analyzed; fluctuations can shift the stability threshold. For some orientations, KESE can stabilize steps. KESE can also induce mound formation. @FootnoteText@ @footnote 1@Work supported by NSF MRSEC grant DMR 96-32521. @footnote 2@ O. Pierre-Louis, M. R. D'Orsogna, and T. L. Einstein, Phys. Rev. Lett. 82 (1999) 3661; note also M. V. Ramana Murty and B. H. Cooper, preprint. @footnote 3@ See, however, I. L. Aleiner and R. A. Suris, Sov. Phys. Solid State 34 (1992) 809; Z. Zhang and M. G. Lagally, Science 276 (1997) 377; J. G. Amar, Bull. Am. Phys. Soc. 43 (1998) 851 and to be published. @footnote 4@ G.S. Bales and A. Zangwill, Phys. Rev. B 41 (1990) 5500.

4:20pm **SS1+EM+NS-ThA8 Atom-by-Atom Growth: Bonding and Rebonding on Metal Surfaces*, A. Bogicevic,*** Sandia National Laboratories

The bond-order--bond-length concept put forth by Pauling almost 70 years ago has greatly added to our intuitive understanding of atomic-scale bonding in molecules. The basic idea is that the more bonds an atom makes, the weaker and longer each becomes [rebonding]. This concept has been extensively tested, and is routinely used in molecular chemistry today, so one would assume that a similar model for the gas-surface interface would prove useful. In an early first-principles study of Al/Al(100), strong and observable rebonding effects were predicted. Unfortunately, these results are an artifact of some severe modelling compromises imposed by computational limitations. New, fully converged (160-180 atom unit-cells, 36 k-points), first-principles density-functional calculations for a wide variety of homogeneous and heterogeneous metal systems show that, contrary to rebonding theory, addimers (adsorbed atom pairs) do not have longer surface bonds than adatoms, do not reside farther above the surface, and do not meet the rebonding arguments for augmented mobility. Rebonding does contribute to destabilize addimers, but does not explain inherently weak adatom-adatom interactions. I explain the absence of rebonding effects in terms of elastic and electronic contributions to the rebonding energy, and present an alternative explanation for the adatom-adatom bond weakness based on bond frustration. Implications for nucleation and growth of metals will be discussed.@footnote 1@ @FootnoteText@ @footnote 1@ Work at Sandia National Laboratories is supported by the U.S. Department of Energy under Contract DE-AC04-94AL85000. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy.

4:40pm **SS1+EM+NS-ThA9 Diffusion of Lead on the Au(111) Surface Studied by Scanning Tunneling Microscopy and Embedded-Atom Method Molecular Dynamics*, M.C. Robinson,*** Trent University and Queen's University, Canada*; K. De'Bell,* University of New Brunswick in Saint John, Canada*; A.J. Slavin,* Trent University and Queen's University, Canada

Low coverages of Pb deposited on the reconstructed Au(111) surface have been studied with STM and show that the reconstruction strongly influences diffusion and film morphology. Nucleation sites for Pb adatoms are found at the kinks of the reconstruction. For higher coverages, Pb atoms concentrate in the fcc and hcp regions; the elevated transition regions are much less populated. The reconstruction is lifted for some coverage between 0.05 and 0.3 monolayers (ML). For comparison, the Embedded Atom Method-Molecular Dynamics (EAM-MD) method has been used to study diffusion of Pb on both the unreconstructed (flat) and reconstructed surfaces. EAM-MD simulations show that diffusion is complicated by the reconstruction. Using both static and dynamic methods, the diffusion energies have been determined. They show that, for an adatom moving perpendicular to the compression direction, the energy barrier is 1.7 times greater than for motion in the parallel direction. Diffusion is slowed on the fcc part of the reconstructed surface, as compared to the unreconstructed, by a factor of about 2. No greater coverage than 0.07 ML could be forced onto the EAM-modelled reconstructed surface. However, the flat surface could be fully covered, suggesting that the reconstruction is not energetically stable at higher coverages, as has been observed experimentally.

5:00pm **SS1+EM+NS-ThA10 Low Energy Electron Microscope Investigation of Pb Overlayers on Cu(100)*, G.L. Kellogg,*** Sandia National Laboratories

Pb overlayers on Cu substrates provide a model system for investigating epitaxial films exhibiting large lattice misfits and for studying two-dimensional phase transitions (e.g., disordering and surface melting). On Cu(100), room-temperature deposition of Pb follows classical Stranski-Krastanov growth with three well-defined overlayer structures forming at submonolayer coverages.@footnote 1@ In this investigation, low energy electron microscopy (LEEM) is used to (1) characterize the changes that occur to these structures resulting from annealing to various temperatures and (2) monitor the subsequent growth of 3-D islands. The low-coverage c(4x4) and high-coverage c(5@sr@2x@sr@2)R45 phases, both of which consist of rotationally inequivalent domains, are observed to disorder at temperatures of 270C and 215C, respectively. By forming images using selected low energy electron diffraction beams (i.e., dark-field LEEM), the domain structure that forms upon cooling from above the transition temperature is imaged directly with a spatial resolution of ~10 nm. Dark-field LEEM is also used to characterize the c(4x4) - c(2x2) co-existence structure that forms upon desorption of excess Pb from the high-coverage phase. The growth of three-dimensional Pb islands on top of the high-coverage phase and the coarsening of these structures at temperatures from 100-150C are measured to derive fundamental energetic parameters involved in the melting of 3-D Pb clusters. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the U. S. DOE under Contract DE-AC04-94AL85000 @FootnoteText@ @footnote 1@ J. Henrion and G. E. Rhead, Surface Sci. 29(1972)20.

Surface Science Division
Room 607 - Session SS2-ThA

Adsorption at Surfaces

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

2:00pm **SS2-ThA1 Dissociative Adsorption of H@sub 2@ on Si(001): Reaction Channels and Structure Sensitivity*, M.B. Raschke*,** *M. Dürr, U. Höfer,* Max-Planck-Institut für Quantenoptik, Germany

Making use of the high adsorbate sensitivity of second-harmonic generation (SHG) the dissociative adsorption of H@sub 2@ on Si(001) could be detected in previous experiments.@footnote 1@ The extremely small sticking coefficients were found to exhibit a pronounced dependence on surface temperature, which indicates the importance of dynamic lattice distortions. In the present investigations, by preadsorbing atomic hydrogen, configurations are realized where, e.g., one of the two dangling-bonds per dimer becomes hydrogen terminated. In contrast to the dissociation on the initially clean Si(001) surface this preparation scheme facilitates two additional inter-dimer reaction pathways occuring with either a neighboring identical half-hydrogen-terminated dimer in the cis-configuration or a clean Si-dimer. Studying the dependence of the reactivities with kinetic energy of the H@sub 2@ molecules using molecular beam techniques, in the first case the dissociation was found to be non-activated, whereas a barrier of 0.2 eV was determined for the second. Together with the barrier of 0.8 eV found for dissociation on the clean surface this corresponds to differences in reactivity up to seven orders of magnitude for a surface temperature of 400 K. Comparing the activation with surface temperature with the dependence on H@sub 2@ beam energy a complementarity between exciting surface and molecular degrees of freedom was found. These results are particularly remarkable because of the geometric similarities of the different configurations of the Si-atoms involved. This together with the results of the recent study of the dissociation at D@sub B@-steps on Si(001)@footnote 2@ provide a systematic understanding of the parameter governing the H@sub 2@/Si(001) interaction. @FootnoteText@ @footnote 1@P. Bratu, K.-L. Kompa, and U. Höfer, Chem. Phys. Lett. 251 (1996) 1. @footnote 2@P. Kratzer, E. Pehlke, M. Scheffler, M. B. Raschke, and U. Höfer, Phys. Rev. Lett. 81 (1998) 5596.

2:20pm **SS2-ThA2 Adsorption of Molecular Hydrogen on the Si(100)-2x1 Surface***, J.J. Boland, **E.J. Buehler**,* University of North Carolina

The mechanism of molecular hydrogen adsorption on the Si(100)-2x1 surface was studied using variable temperature scanning tunneling microscopy. The measured desorption barrier of ~2.5eV and the bond energies of Si--H (3.5eV) and H--H (4.5eV) predict a tiny barrier to adsorption. This agrees with data showing that desorbing molecules have no excess translational energy as they leave the surface. The magnitude of the room temperature sticking coefficient (<10@super -10@), however, shows that there is actually a large barrier to adsorption, suggesting a violation of detailed balance. We show that the origin of this discrepancy lies in the motion of the atoms of the Si dimers. The dimers of the clean Si(100)-2x1 surface are constantly tilting at room temperature. We have prepared a surface that contains clean Si--Si dimers that are frozen in a relatively untilted configuration. The room temperature sticking coefficient of molecular hydrogen at these sites is six orders of magnitude greater than that on a clean Si(100)-2x1 surface. The implications for hydrogen adsorption and detailed balance are discussed.

2:40pm **SS2-ThA3 Molecular Beam Study of the Adsorption and Desorption of Hydrogen Sulfide on Au(100)***, **St.J. Dixon-Warren**,* Washington State University

The adsorption and desorption of hydrogen sulfide on clean reconstructed Au(100)-(5x20) and sulfided gold, denoted Au(100)-(1x1)-SH, has been studied with a combination of temperature programmed desorption (TPD), low energy electron diffraction (LEED), Auger electron spectroscopy (AES) and molecular beam methods. Precursor adsorption kinetics were observed for the adsorption of H@sub 2@S on the Au(100)-(5x20) between 80 and 100 K. The H@sub 2@S adsorbs reversibly into a weakly bound physisorbed state, which desorbs at ~107 K. At 110 K reversible Langmuir adsorption was observed for H@sub 2@S on the Au(100)-(5x20). The Au(100)-(1x1)-SH was prepared by electron irradiation of H@sub 2@S adsorbed on the Au(100)-(5x20) substrate. The adsorption kinetics for H@sub 2@S on the Au(100)-(1x1)-SH exhibited Langmuir adsorption kinetics at 80 K, in sharp contrast with the precursor adsorption kinetics observed on the clean Au(100)-(5x20) surface. The TPD of H@sub 2@S from Au(100)-(1x1)-SH and H@sub 2@S adsorbed on Au(100)-(1x1)-SH showed additional features at higher temperatures which are probably associated with the disproportionation of chemisorbed HS(ad). Finally, we have identified a further sulfided gold surface, denoted Au(100)-(2x2)-S which is prepared by annealing the Au(100)-(1x1)-SH to remove adsorbed hydrogen.

3:00pm **SS2-ThA4 Decomposition of Nickelocene on Single Crystal Surfaces***, **D.L. Pugmire**, C.M. Woodbridge, M.A. Langell,* University of Nebraska, Lincoln

The decomposition mechanisms of nickelocene on several surfaces of varying reactivity have been elucidated by use of high resolution electron energy loss spectroscopy (HREELS), x-ray photoelectron spectroscopy (XPS), and temperature programmed desorption (TPD). Exposure of nickelocene to the reactive Ni(100) surface at 135 K results in its decomposition into fragments containing C-C triple bonds. When this substrate is warmed to 273 K, carbide contamination is observed. Exposure of nickelocene to NiO(100) at 135 K also yields decomposition, but with different products than those observed on Ni(100). There is no evidence for the formation of species containing C-C triple bonds on NiO(100). Instead, species with C-C double bonds result upon adsorption at 135 K and as the NiO(100) substrate is warmed to 273 K, all carbon-containing species desorb. In contrast to the reactive nature of Ni(100) and NiO(100), Ag(100) molecularly adsorbs nickelocene at 135 K with its molecular axis perpendicular to the substrate surface. When this substrate is heated, nickelocene desorbs molecularly at approximately 210 K, leaving a surface free of residual carbon. Mechanisms of nickelocene decomposition on the reactive surfaces are proposed based on the HREELS, XPS and TPD results.

3:20pm **SS2-ThA5 New Opportunities in Surface Studies using High Brilliance Synchrotron Radiation***, **N. Mårtensson**,* Uppsala University, Sweden **INVITED**

Synchrotron radiation is a most powerful source for electromagnetic radiation with wide applications in a variety of research areas. With synchrotron radiation one can span in a continuous manner a large photon energy range. The radiation is intense and stronly polarized, linearly or circularly. The third generation synchrotron radiation sources which are now coming into operation are optimized for the utilization of insertion devices, i.e. undulators and wigglers, in the straight sections of the storage rings. The utilization of resonant spectroscopies will be discussed. The element specificity at core level thresholds can be used to focus on specific elements or even chemically different species of the same element in complex environments, e.g. at buried interfaces or in adsorbed molecules. The utilization of such techniques will be discussed in different regimes of the electronic structure. The characterization of the electronic states in CuNi systems will be discussed. Resonant photoemission, autoionization or resonant x-ray scattering also allow one to study dynamic properties of the excited states, e.g. probing charge transfer processes between weakly adsorbed molecules and surfaces. It is also shown how X-ray photoelectron spectroscopy at a resolution of 50 meV of adsorbed molecules make it possible to resolve vibrational fine-structure, thereby enhancing the information contents in the spectra considerably. The new way of studying chemical bonding at surfaces using x-ray emission spectroscopy will also discussed

4:00pm **SS2-ThA7 The Surface Chemistry of Iron Pentacarbonyl on Palladium (111)***, **M.N. Rocklein**, D.P. Land,* University of California, Davis

The interaction of organometallic compounds with surfaces can lead to catalytically-active surface moieties or to metal deposition. This is important to industries concerned with supported metal catalysts, magnetic storage, and microelectronics. Depending of the exposure, iron pentacarbonyl desorbs from the close-packed palladium surface in ultra-high vacuum at 153 and 170 K. This corresponds to multilayer and saturation coverage desorption. However, approximately 30% of the first saturation layer decomposes on the surface during the temperature programmed desorption (TPD) experiment. This implies that some reaction was initiated below 170 K. Laser-induced thermal desorption Fourier transform mass spectrometry (LITD-FTMS) is capable of showing time-resolved changes in molecular surface composition. Interestingly, LITD shows that submonolayer coverages react at 150 K with further decomposition near 200 K. This study represents the first LITD-FTMS temperature survey of an organometallic/substrate system. TPD further shows evolution of carbon monoxide by a reaction-limited process near 260 K. The simplest explanation of this behavior involves a stepwise decarbonylation and the existence of surface intermediates up to at least 260 K. The proposed mechanism is further supported using reflection-absorption infrared spectroscopy (RAIRS).

4:20pm **SS2-ThA8 Adsorption Driven Displacement of N@sub 2@ from Pt(111)***, **G.A. Kimmel**, K.P. Stevenson, B.D. Kay,* Pacific Northwest National Laboratory

Pt(111) with beam reflection measurements and temperature programmed desorption (TPD). The interaction of weakly adsorbed species on surfaces is of fundamental interest since these systems provide a benchmark for more complicated systems. Our experiments involve the preparation of monolayer or sub-monolayer coverages of N@sub 2@ on Pt(111) followed by the adsorption of another species (e.g. CH@sub 4@, Kr and H@sub 2@O). Both species are monitored throughout the experiments, allowing for quantitative measurements of the coverages and sticking coefficients versus time. In all cases, N@sub 2@ is displaced from direct contact with the Pt(111) by the adsorbates which have higher binding energies. The fate of the displaced N@sub 2@ molecules is governed by the surface temperature and its interaction energy with the co-adsorbate. At higher temperatures, the N@sub 2@ desorbs as soon as it is displaced from the first layer. As the temperature is lowered, the N@sub 2@ desorbs when it is displaced from successively higher layers. This behavior results from the successively lower binding energy of N@sub 2@ to increasingly thick co-adsorbate layers. At "high" temperatures (~38 K), the N@sub 2@ desorption rate is approximately constant during the adsorption of the first monolayer of CH@sub 4@, falling abruptly to zero with its completion. This suggests that the mobility of the adsorbed CH@sub 4@ is high allowing it to rapidly find and displace N@sub 2@. The CH@sub 4@ sticking coefficient increases linearly with time as the surface layer is converted from N@sub 2@ to CH@sub 4@. TPD subsequent to the CH@sub 4@ exposure shows that the entire N@sub 2@ monolayer was displaced and desorbed during the CH@sub 4@ adsorption. At lower temperatures, lower diffusion rates lead to departures from zero-order desorption kinetics. The displacement of N@sub 2@ by H@sub 2@O is qualitatively similar, but quantitative comparisons are complicated by details of the N@sub 2@/H@sub 2@O interaction.

4:40pm **SS2-ThA9 The Vibrational Spectra of Adsorbed Alkoxies on Cu(100) and W(110): Experimental Data and ab initio Calculations***, **P. Uvdal**, R. Ásmundsson,* Lund University, Sweden*; A.D. McKerell, Jr.,* University of Maryland

Using surface FTIR spectroscopy we have measured the vibrational spectra of different alkoxies adsorbed on single crystal surfaces of Cu(100) and W(110). It is demonstrated how modification of the alkyl chain and the associated changes in the experimental vibrational spectra can be calculated with a high degree of accuracy using ab initio electronic structure calculations of an alkoxy-metal complex as the model. Analysis of the symmetry properties of the calculated normal modes allows for a determination of the geometry of the adsorbed species.

5:00pm **SS2-ThA10 Probing the Metal Sites of a V-oxide/Pd(111) "Inverse Catalyst": Adsorption of CO***, F.P. Leisenberger, G. Koller, S. Surnev, M.G. Ramsey, **F.P. Netzer**,* Karl-Franzens-Universität Graz, Austria

A vanadium oxide / Pd(111) "inverse catalyst" system, consisting of V-oxide island structures and bare Pd(111) patches in between, has been prepared by reactive evaporation of V onto Pd(111) at submonolayer to monolayer coverages and has been characterised by STM and high-resolution core level photoelectron spectroscopy. Here we report a study of the adsorption of CO on these "inverse" V@sub 2@O@sub 3@/ Pd(111) catalyst. Since CO does not adsorb on V-oxide at room temperature, this allows to probe the adsorption properties of free Pd(111) sites in the presence of the V-oxide phase boundary. The adsorption of CO has been followed by monitoring the C 1s core level signals as a function of the V-oxide coverage and the CO exposure at room temperature, using high-resolution XPS with synchrotron radiation. The amount of adsorbed CO, as determined quantitatively from the C 1s peak areas, decreases with the V-oxide coverage as a result of the blocking of Pd adsorption sites. The concomitant decrease of the CO saturation exposure, i.e. the CO exposure necessary to reach CO saturation of the various surfaces, indicates, however, that a precursor state exists on the V-oxide surface, from which CO can diffuse over the metal-oxide boundary on to Pd sites. This spill-over effect is also corroborated by the dependence of the initial sticking probability of CO on the V-oxide surface coverage. The difference of the C 1s binding energies of CO adsorbed on pristine and oxide covered Pd(111) suggests that Pd adsorption sites are electronically influenced by the presence of a V-oxide phase boundary. Supported by the Austrian Science Foundation.

Surface Science Division
Room 613/614 - Session SS3+BI-ThA
Biological Surface Science

Moderator: B. Kasemo, Chalmers Univ. of Tech. and Göteborg Univ.

2:40pm **SS3+BI-ThA3 Thia(Ethylene Oxide) Alkanes: Tuning the Structure of a Supported Biomimetic Membrane via Spacer Length and Packing Density***, D.J. Vanderah, C.W. Meuse, T. Petralli-Mallow, **A.L. Plant**,* National Institute of Standards and Technology **INVITED**

Interest in reconstituting transmembrane proteins in supported cell membrane mimics of phospholipid/alkanethiol hybrid bilayers has led to development of novel tethering molecules. In an attempt to introduce a disordered, hydrophilic region at the proximal side of the supported lipid bilayer, ethylene oxide moieties have been used as spacers between the sulfur and the alkane chain of alkanethiols. We have observed by infrared spectroscopy, neutron reflectivity, and electrochemistry that such ethyleneoxide moieties are not necessarily hydrated or disordered. The ethylene oxide of thiahexa(ethylene oxide) alkanes (HS(EO)@sub 6@-alkanes) form a highly ordered arrangement of 7/2 helices when allowed to self-assemble at gold from an ethanolic solution. This highly ordered conformation is apparently not driven by order in the alkane chains, since the helical structure occurs in both HS(EO)@sub 6@-decane and HS(EO)6-octadecane. The conformation is, however, determined in part by molecular density. Infrared analysis of mixed monolayers of HS(EO)@sub 6@-alkanes and phospholipids transferred from the air-water interface indicates that at low packing densities the EO region is disordered, but it assumes the helical structure at higher packing densities. Infrared spectroscopy and sum frequency generation suggest that the conformation of the EO region may be controlled by its length. For a series of self-assembled monolayers of HS(EO)@sub n@-decanes, the EO segment is an extended all-trains chain when n=4, a 7/2 helix when n=5-7, and a less ordered conformer when n=8. This effect of spacer length and packing may provide a means of tuning the molecular order of biomimetic matrices.

3:20pm **SS3+BI-ThA5 Quantitative Analyses of Biological Interactions using Surface-Biofunctionalized Surface Plasmon Resonance Devices***, **C.T. Campbell**, L.S. Jung, J. Shumaker-Parry, K.E. Nelson, P.S. Stayton, M.S. Boeckl, M.H. Gelb, S.S. Yee, T. Sasaki, R. Aebersold,* University of Washington **INVITED**

The adsorption of molecules from liquid solutions onto solid surfaces can be monitored with high sensitivity and fast time response by following changes in the angle or wavelength at which the surface plasmon resonance (SPR) of a thin metal film is optically excited. Simple methods convert these measured changes into adsorbate concentrations. We report here the adsorption and desorption kinetics and equilibrium coverages of a variety of species on well-characterized surfaces as determined by SPR techniques. When the diffusion constant of the adsorbing species is known in the liquid phase, the intrinsic rate constants can be determined from the kinetic results. A new method will be described for converting intrinsic adsorption rate constants into sticking probabilities (i.e., the probability that adsorption occurs, given a collision of the molecule with the surface). Several applications of gold-thin-film SPR sensors in quantifying biological interactions will be described. A gold surface containing a few biotin headgroups in a self assembled alkylthiol monolayer of mainly oligo(ethylene glycol) headgroups has been used to assess the effects of protein mutations on the strength of biotin-streptavidin binding. With wild-type streptavidin, the free biotin sites in the resulting streptavidin monolayer have been used as strong linker sites for further attachment of intact, biotinylated lipid vesicles and biotinylated, double-stranded oligonucleotides to the surface. These complex biological films then provide a surface template that can be used to probe the kinetics and equilibrium binding constants for: (1) peripheral membrane proteins binding to vesicle walls, and (2) the binding of DNA-binding proteins to select oligonucleotide sequences.

4:00pm **SS3+BI-ThA7 Adsorption and Reactions in Enzymes and on Surfaces: Similarities And Differences***, A. Logadottir, T.H. Rod,* Technical University of Denmark*; **J.K. Nørskov**,* Technical University of Denmark, Denmark **INVITED**

There are a number of cases where surfaces and biomolecules adsorb the same molecules and catalyze the same reactions. This makes it possible to make comparisons and to see if the concepts of surface science can be transferred to biomolecules. As a specific example, the adsorption of N@sub 2@ and the ammonia synthesis reaction on metal surfaces and in the enzyme nitrogenase will be compared in detail. The comparisons are largely based on density functional calculations which provide a detailed description of the extensive database of experiments for the nitrogen activation process on Fe and Ru surfaces, and which can be used to give the first hint of a mechanism in the enzyme process.

4:40pm **SS3+BI-ThA9 The Role of Hydrogen Bonding in Chemisorbed Aminoacids***, **N.V. Richardson**,* University of St Andrews, UK **INVITED**

Glycine and its derivatives such as phenyl glycine and alanine form well-ordered monolayers of the corresponding anion on Cu(110). The unit cells reflect both the strong adsorbate-substrate interaction and the hydrogen bonding interactions between adsorbed species. In the case of the chiral amino acids studied, this leads to ordered domains of the two isomers which are distinguishable. Glycine undergoes several orientational changes during the build up of the ordered monolayer and is then able to form a stable bilayer. Such a bilayer is not formed in the case of phenyl glycine or alanine demonstrating the importance of optimal hydrogen bonding in stabilising the bilayer. Adsorption of water on the glycine covered copper surface drives a re-orientation of the molecule which we also relate to the importance of hydrogen bonding between the co-adsorbed species.

Thin Films Division
Room 615 - Session TF-ThA
Ex-situ Characterization

Moderator: J.J. Nainaparampil, Air Force Research Laboratory

2:00pm **TF-ThA1 Working Smarter with Microanalytical Tools*, M.J. Edgell,*** Charles Evans & Associates **INVITED**

New materials development and high yield production lines are key to future generations of integrated circuits (ICs). Material and contamination characterization is therefore an integral part of the semiconductor industry. The capabilities of analytical tools are continuously improving to meet the needs of the National Technology Roadmap for Semiconductors (NTRS). The analytical improvements include electron and ion beam resolution, detector technology, and surface sensitivity. This paper reviews several ex-situ analytical tools, such as AES, RBS, SIMS, SEM, SIMS, TXRF, TOF-SIMS, XPS, used in today's high technology industries. The strengths and weaknesses of the techniques and their applications will be discussed.

2:40pm **TF-ThA3 Near Surface Chemical Dependence of Electronic States at Al-Doped TiO@sub 2@(110)Ultrathin Films*, S.H. Goss,*** *L. Brillson,* Ohio State University*; S.A. Chambers,* Pacific Northwest National Laboratory

Impurity doping of TiO2 has important catalytic and photocatalytic applications.@footnote 1@ Al doping is known to enhance TiO2's chemical properties and is used extensively in surface coatings. We have used electron excited nanoscale luminescence spectroscopy (EENLS) to observe the dependence of electronic states with chemical composition of Al-doped TiO2 ultrathin films. Using incident electron beams of varying energy to probe depths from 150 nm below the free surface, we observe: mid-gap state emission at 1.4 eV due to Al doping, O vacancy emission at 2.5 eV, and near band edge (NBE) transitions at 3.0 eV. The 1.4 eV emission appears specifically within a 20 nm, 6% Al - doped TiO2 layer stacked on 4% and 2% doped layers, all grown epitaxially on TiO2 substrates. No 1.4 eV emission is evident for these deeper layers. Recombination involving this 1.4 eV level increases dramatically with annealing at 600 C under 5-x 10e7 L O2 treatment, while the 2.5 eV peak decreases. As mid-gap recombination increases, NBE emissions decrease strongly, indicating a pronounced decrease in free carrier concentration near the free surface. Auger electron spectroscopy (AES) shows Ti and O in correct proportion and only C contamination at the free surface. Mid-gap emission intensities show no correlation with surface C concentration which range from

3:00pm **TF-ThA4 Microstructure and EL Properties of the ZnS:Mn Luminescence Materials with Co-dopants*, Q. Zhai,*** *K.E. Waldrip, J. Li, J.S. Lewis, K. Jones, P.H. Holloway,* University of Florida*; M. Puga-Lambers, M. Davidson,* MICROFABRITECH

ZnS:Mn thin films were deposited onto glass substrate with pre-deposited indium tin oxide (ITO) and aluminum titanium oxide (ATO) layers, using magnetron sputter source. Transmission electron microcopy (TEM) indicated that the microstructure of the as-deposited films was heavily faulted with fine columnar grains formed through most of the film and a 100nm layer of equiaxed fine grains at the ATO/ZnS:Mn interface. The electroluminescence (EL) properties of the as-deposited films were poor. Post deposition rapid thermal annealing (RTA) with and without co-dopants was studied. KCl co-doped samples showed remarkable improvement in EL brightness after an RTA of 5 min. at 700@super o@C. The threshold voltage was slightly increased. Grain growth from 80nm as-deposited to 200nm after RTA was observed, and the fine-equiaxed-grain crystal layer was removed. Energy dispersive X-ray (EDX) spectra analysis of plan-view transmission electron microscoy (PTEM) samples detected no segregation of any element. Ga@sub 2@S@sub 3@ co-doped samples had no improvement in EL brightness after 5 min. RTA at 800@super o@C, but the threshold voltage was reduced. Grain growth was less than the samples without Ga@sub 2@S@sub 3@, and the fine-equiaxed-grain layer was still visible. EDX results showed Ga segregation at grain boundaries and triple points. When both KCl and Ga@sub 2@S@sub 3@ were introduced into the films through double thermal evaporation/annealing, the sample co-doped with Ga@sub 2@S@sub 3@ at 800@super o@C followed by KCl at 700@super o@C gave the best EL results, but the properties were still inferior to the samples with only a KCl treatment. EDX on PTEM samples detected both K and Ga segregated to grain boundaries and triple points of these samples. The diffusion of co-dopants was analyzed by dynamic secondary ion mass spectrometry (SIMS). Detailed electrical properties of these samples are being studied. A correlation between EL properties and the microstructure will be presented.

3:20pm **TF-ThA5 Structural Determination of Wear Debris Generated from Sliding Wear Tests on Ceramic Coatings Using Raman Microscopy*, C.P. Constable,*** *J. Yarwood, P. Hovsepian, L.A. Donohue, W.-D. Münz,* Sheffield Hallam University, UK

During sliding, the high pressure at the point of contact can contribute to high flash temperatures, which are not accurately measurable. The magnitude of these flash temperatures has been quoted as being up to several hundred degrees Celsius for some systems but remains a topic for debate. Tribologists interested in ceramic coatings are realising that the wear debris can bear the signature of the wear process and the composition of the debris can enable an estimate of these contact temperatures. Raman microscopy is utilised here for the identification of compounds, especially oxides, generated during the wear process to endeavour to gain a better understanding of tribochemical reactions. A series of PVD ceramic hard coatings; CrN/NbN, CrN, NbN, TiAlN/VN, TiAlCrYN and TiCN have been deposited on steel substrates using the cathodic arc/unbalanced magnetron deposition technique. Ball-on-Disk sliding wear tests against corundum were performed for all the above coatings. The debris generated were characterised using vibrational spectroscopy; namely Raman microscopy. The high spatial resolution (2µm), in-situ capability, sensitivity to structural changes and non-destructive nature make this technique ideal for the study of such small amounts of wear debris. Previous work has centred on TiN coatings. This paper attempts to broaden the discussion to include other more complex monolithic and multilayered superlattice coatings. Under dry sliding conditions of 5N normal load, 10cms@sup -1@ in ambient air (humidity ~33%) titanium based alloy coatings were found to provide TiO@sub 2@ (rutile) debris. However the addition of fine layers of VN to the TiAlN system provided lower friction coefficient, wear rate and less debris through the possible formation of a lubricious surface oxide. CrN and NbN based coatings were also found to produce debris with Raman bands corresponding to various oxides.

3:40pm **TF-ThA6 Effect of Rapid Thermal Annealing Temperature on the Formation of CoSi Studied by X-ray Photoelectron Spectroscopy and Micro Raman Spectroscopy*, J. Zhao,*** *L. Ballast, T. Hossain, R. Trostel, B. Bridgman,* Advanced Micro Devices

Silicides are widely used on poly-Si as low resistance gate electrodes and local interconnects. Among all silicides, CoSi@sub 2@ attracts a special interest, not only because of its low resistance and its technical advantages in processing, but also its excellent match with Si. CoSi is the intermediate phase in the conversion sequence of pure Co, CoSi and CoSi@sub 2@. In this paper, we investigated the effect of rapid thermal annealing (RTA) temperature on the formation of CoSi using X-ray photoelectron spectroscopy (XPS) and micro Raman spectroscopy. With pure Co deposited on single crystalline Si wafer and capped by Ti thin film, the wafers were rapid thermal annealed at 450, 460, 470, 480 and 490@super o@C, respectively. These wafers were then stripped with SPM (H@sub 2@SO@sub 4@/H@sub 2@O@sub 2@). XPS was used to determine the chemical composition of the CoSi thin films and Auger parameter was continuously monitored along with ion sputtering to provide chemical state depth profile. XPS depth profile shows that uniform CoSi film was developed with RTA at 470@super o@C. The wafer with RTA at 450@super o@C has a pure Co layer in between the CoSi film and Ti cap. After strip, the thinnest CoSi film was observed with this wafer among the five. On the other hand, the wafer with RTA at 490@super o@C shows significant amount of Ti diffusion into the CoSi film. After strip, XPS depth profile indicates that this wafer has residue Ti on the top of CoSi surface. Micro Raman spectroscopy was used as a non-destructive method to characterize the film thickness and uniformity of the CoSi films on Si wafer. The product, @theta@d (@theta@ - absorption coefficient, d - film thickness) was calculated from both the Si excitation wavelength of 521cm@super -@ and CoSi excitation wavelengths of 206cm@super -@ and 224cm@super -@. The correlation of the measured Raman peak intensity ratio, the calculated product @theta@d and the sheet resistance of CoSi thin film were also elucidated.

4:00pm **TF-ThA7 Optical Metrology for Process Development and Control of Universal Anti-Reflective Layers*, J.M. Holden,*** Nanometrics, Inc.*; Y. Wang, Z. Karim, K. MacWilliams,* Novellus Systems

A two-layer, inorganic anti-reflective layer (ARL) consisting of a high extinction coefficient SiO@sub x@N@sub y@ bottom layer and a low extinction coefficient SiO@sub x@N@sub y@ top layer is used as a "Universal" ARL or UARL. The UARL is useful in damascene lithography or anywhere substrate reflectance is unknown or uncontrollable. The optical dispersions of individual films of the structure are characterized by Variable

Angle Spectroscopic Ellipsometry (VASE@footnote 1@). Minimal parameter models are used to describe refractive index, n(@lambda@), and extinction coefficient, k(@lambda@), dispersions for top and bottom films. The dispersion models are implemented on a metrology tool that uses combined reflectance and spectroscopic ellipsometry (R+SE). Quantities relevant to DUV lithography, n(248 nm), k(248 nm), and thickness, t, are measured identically by VASE and R+SE methods. The metrology tool was used for process development and is applicable to process monitoring in a fab environment. Individual films are deposited as either a single film deposited on a single deposition station (static) or deposited in a multi-station, sequential deposition. The effect of interface layers in the sequentially deposited films can be detected weakly from ellipsometric data but not from reflectance. Normal incidence reflectance measurements and lithography simulations for typical DUV exposure tools indicate no significant differences between static and sequentially deposited films. @FootnoteText@ @footnote 1@VASE is a trademark of the J. A Woollum Company.

4:20pm **TF-ThA8 Temperature Dependence of Structure and Electrical Properties of Germanium-Antimony-Tellurium Thin Films***, J. González-Hernández,* ***E. Prokhorov****, Y.V. Vorobiev,* Centro de Investigacion y de Estudios Avanzados del IPN, Mexico

The interest in the study of Ge:Sb:Te thin films is due to their use as optical and electrical devices materials. Both of these applications are based on structure change from amorphous to crystalline. Thus, understanding of the mechanism of crystallization in this material is important from the basic technological point of veiw. In this work we have studied the kinetics of the crystallization of Ge:Sb:Te films prepared by thermal evaporation. For that, in situ resistance and capacitance measurements during heating were used. The transformation kinetics from amorphous to crystalline phase was analyzed on the basis of the annealing behavior. The results were interpreted using Kissinger model, from which, the activation energy of the crystallization process is obtained. Using X-ray diffraction, Raman spectroscopy and optical microscope measurements, we have observed that during heating at different heating rates, crystallization of film is accompanied by Te phase segregation. The number and size of Te inclusions depend on the heating rate and film thickness. From our measurements we found that the capacitance measurements is the new highly sensitive method to control the crystallization process in the thin films. It provides additional information not obtained using other methods.

Applied Surface Science Division
Room 6A - Session AS-FrM

New or Improved Surface Related Analytical Techniques
Moderator: P.M.A. Sherwood, Kansas State University

8:20am **AS-FrM1 LEIS Measurement of Target Mass in the Presence of Inelastic Energy Losses@footnote 1@*, R. Bastasz*,** *J.A. Whaley,* Sandia National Laboratories

Low-energy ion scattering (LEIS) is often used to identify the elements present on a surface. Peaks observed in the energy spectrum of scattered ions can be assigned to specific target masses. However, the usual kinematic expression that relates the energy of a scattered projectile to a target atom mass does not account for inelastic losses, such as ion neutralization/reionization and excited state formation, which can significantly affect the scattered-ion energy. We have developed a simple method for unambiguously determining target atom mass from LEIS measurements regardless of the amount of inelasticity in the collision. Analysis of the scattering kinematics with an included inelastic loss term shows that the scattered particle velocities form a circle in the polar coordinate system (v@sub n@,@theta@), where v@sub n@ is the normalized scattered-ion final velocity and @theta@ is the laboratory scattering angle. While the circle radius changes with the degree of inelasticity, the circle center depends only on the target-to-projectile mass ratio. So, by measuring ion energy spectra at three or more scattering angles, it is possible to construct the appropriate scattering circle, find its center, and deduce the target mass. The only assumption in the method is that inelastic losses are not a function of the impact parameter. This assumption appears reasonable at typical observation angles, as can be illustrated with several examples of inert-gas scattering from low-Z metal surfaces. @FootnoteText@ @footnote 1@ This work was supported by the US Department of Energy under contract DE-AC04-94AL85000.

8:40am **AS-FrM2 Atmospheric Electron X-ray Spectrometer*, J. Feldman,*** *J.Z. Wilcox, T. George,* Jet Propulsion Laboratory*; D.N. Barsic, A. Scherer, T. Doll,* Caltech

Atmospheric Electron X-Ray Spectrometer (AEXS) J. Feldman, J. Z. Wilcox, and T. George, Jet Propulsion Laboratory D. N. Barsic, T. Doll, and A. Scherer, Electrical Engineering and Applied Physics, Caltech Abstract The Atmospheric Electron X-ray Spectrometer (AEXS) is a new miniature instrument being developed for in situ elemental analysis of surfaces. The key component of the instrument is a microfabricated silicon nitride membrane. This electron transmissive membrane serves to isolate the high-vacuum electron column from the ambient atmosphere. An electron beam generated and focused in the column is transmitted through the membrane to impinge on the sample in the ambient atmosphere. The electron beam excites characteristic x-rays, which are analyzed to determine the elemental composition of the irradiated portion of the sample. The power of this type of analysis is that samples can be analyzed in situ without being introduced into a vacuum chamber as in traditional scanning electron microscopy (SEM). Due to the return ionization path through the atmosphere, sample preparation is unnecessary even for non-conductive samples. This talk describes the development and current status of the AEXS. Initial spectra were obtained in ambient Earth atmosphere with a spot size of less than 1mm and a spectrum acquisition time of a few minutes. The physical properties of a number of candidate low atomic number microfabricated membranes, including electron and x-ray transmissivity, will be discussed. The prototype instrument is designed to be portable, with a mass of 1 kg. The high spatial resolution of the AEXS (as compared to alpha particle or x-ray fluorescence instruments) will enable mapping of compositional heterogeneities at a grain size level. In addition to applications in planetary exploration, the AEXS also has potential applications in industrial process monitoring and quality control.

9:00am **AS-FrM3 Advances in X-ray Photoemission Spectroscopy at Very High Spatial and Spectral Resolution*, B.P. Tonner*,** *R. Kneedler,* University of Central Florida*; K. Pecher,* California Institute of Technology*; T. Warwick,* Lawrence Berkeley National Laboratory **INVITED**

Soft x-ray undulator synchrotron radiation has resulted in dramatic improvements in the performance of x-ray photoemission spectroscopy (XPS)for the study of surfaces and shallow interfaces. The two main areas of improvement are in spatial resolution and spectral resolution, which, in combination, result in improved sensitivity of the technique. Recent work with complex surfaces, such as the surfaces of natural minerals, will be used to show that fundamental issues regarding surface composition of such materials can be resolved using XPS imaging and spectroscopy from sub-micron areas. XPS microscopy is used to qualify surfaces for further analysis using high resolution photoelectron diffraction (XPD). XPD studies of large unit cell surfaces, and of mineral surfaces, will be selected to illustrate the precision of atomic geometry that can be determined. Examples will be drawn primarily from our work on copper sulfide, bixbyite, galena, and pyrite surfaces.

9:40am **AS-FrM5 An Evaluation of the ALS Micro-ESCA Beam Line Performance for Small Particle Analysis*, C.R. Brundle*,** *Y. Uritsky, G. Conti,* Applied Materials, Inc.*; P. Kinney,* MicroTherm, LLC*; Y. Ynzunza,* Intel Corporation*; E. Principe,* Charles Evans and Associates

Intel, Applied Materials, and the ALS synchrotron staff have developed a micro-ESCA beam line at the Advanced Light Source, LBL. One of the major objectives was to produce "user-friendly" analysis at a spatial resolution significantly beyond that available in commercial instrumentation. We review the status of the project using both test structures and real particle situations and conclude the following: 1) Usable signal intensities are attainable down to ~2 µm size features, the nominal X-Ray beam size. This is 5 to 10x better than the PHI Quantum 2000. 2) The sample handling and navigation system to find small features works well (considerably better than any commercially available approach on ESCA systems). 3) The availability of the NEXAFS operation mode, in addition to the ESCA mode, provides valuable additional chemical state delineation capabilities. 4) Charging issues for insulating films and particles need to be resolved. 5) Since the "turn-around" analytical time and spatial resolution will always be far worse than for commercial SAM, the practical usefulness of the beam line depends strongly on its enhanced capability, compared to SAM, for chemical state delineation using the ESCA chemical shifts and near-edge structure, and on the reduced beam effects compared to e-beam SAM.

10:00am **AS-FrM6 A Study of TOF-SIMS for the Analysis of Metal Contamination on Silicon Wafers*, I.A. Mowat*,** *T.J. Schuerlein, J. Metz, R. Brigham, D. Huffaker,* Charles Evans & Associates

The current methods of choice for the analysis of metal contaminants on silicon wafers are Total Reflection X-Ray Fluorescence (TXRF) and SurfaceSIMS. TXRF is a survey technique, with good detection limits for transition metals (e.g. down to 10@super 9@atoms/cm@super 2@ for some elements). SurfaceSIMS is not usually used as a survey technique, but it has high sensitivity for species such aluminum and alkali metals (species not detected well by TXRF). Time-of-flight SIMS (TOF-SIMS) is a technique which offers a surface survey of all metal contaminants, with good detection limits. This paper details the investigation of TOF-SIMS as a possible tool for such analyses. Under the high beam current conditions used, elemental information is obtained with high sensitivity (under certain conditions, the detection limit for iron can be below 10@super 9@atoms/cm@super 2@, and is much lower for the alkali metals). Experiments were carried out to investigate the accuracy and precision of TOF-SIMS analyses of Si wafers. The areas of interest were: (1) short term variability of data from a standard spin coated wafer; (2) long term variability (over approximately six months) of data from the same wafer; (3) investigation of factors affecting the detection limits achievable by TOF-SIMS; (4) cross correlation of TOF-SIMS with established techniques such as TXRF and SurfaceSIMS. Short term variability was determined to be in the range 10-12%, and long term variability was ~20%. Work is underway to investigate the sources of this variability. Detection limits were studied by assessing wafers from different sources in the semiconductor industry, and were found to vary by up to a factor of five. Cross correlation with both TXRF and SurfaceSIMS have proven to be a good source of information to increase the accuracy of TOF-SIMS measurements. The information obtained will help assess the suitability of TOF-SIMS as an additional method for metal contamination measurement on silicon wafers.

10:20am **AS-FrM7 Fundamental Studies of Polymer and Protein Cationization by ToF-SIMS*, R Michel*,** *R. Luginbuehl, D.J. Graham, B.D. Ratner,* University of Washington

Cationization of polymers, proteins and polypeptides is carried out on novel substrates with Time of Flight Secondary Ion Mass Spectrometry (ToF-SIMS). The surfaces consist of carboxylic terminated self-assembled monolayers with various metal ions such as Ag, Na, Li, Tl, and Cu substituting the terminal hydrogen. The resulting surfaces are used as carrier substrates for deposition and analysis of polymers, proteins and polypeptides. Low (1 kD) and high (400 kD) molecular weight polyethyleneoxide (PEO) was deposited via spincoating while the proteins were adsorbed to the substrates. Previously published results show that cationization of polymers was achieved with the various selected metal ions from the carboxylic terminated groups. Complementary experiments carried out on non-substituted and methyl terminated self-assembled monolayers suggested that metal ions which are desorbed from the gold surface and therefore not in close proximity to the polymer do not cationize polymers and their fragments. The intensity of the cationized fragments were observed to be dependent on the metal ion used. Both cationized fragments and whole molecular species were observed for the 1kD PEO while on 400 kD PEO chain fragments of up n = 25 monomer units were detected. For protein samples using our substrate, detection of whole low molecular weight proteins up to 2 kD could be achieved with additional peak patterns indicating a loss of peptide- and sidechains.

10:40am **AS-FrM8 Synchrotron TXRF Quantification Using Ion Implanted Standards***, R.L. Opila,* ***J.P. Chang****, J. Eng, Jr., J.R. Rosamilia,* Bell Labs, Lucent Technologies*; P. Pianetta,* Stanford University*; F.A. Stevie, R.F. Roberts, M.A. Decker,* Bell Labs, Lucent Technologies

Much of the difficulty in quantification using TXRF has been associated with problems in obtaining suitable standards. The quantification can be very accurate, but the standards to date are difficult to prepare and are not generally available. Ion implantation is often used for quantification of secondary ion mass spectrometry and can be obtained for any element, but the implanted distribution is not well defined at the surface. The technique of implantation through a sacrificial oxide layer has been applied to create TXRF quantification standards. Ion implants of Ca, Fe, Cu, Ni, As, and Sb were made through 0.1 µmm SiO@sub 2@ on Si substrates. Measurements were made using conventional and synchrotron TXRF after removal of the oxide. The results show that there is a direct correlation between the ion dose and the TXRF measured dose in the sampling depth for TXRF. Measurements were made using surface and time-of-flight SIMS, with similar conclusions. Certain elements, e.g., copper, are known to plate on the surface after oxide etch. One unique advantage of performing TXRF at the synchrotron is the ability to easily change the energy of the exciting x-rays. Using the dependence upon incident photon energy it is possible to collect a near edge absorption spectrum of the metallic species. This near edge spectrum then permits determination of the chemical bonding of the metallic element. By varying the angle of the incident x-rays above and below the critical angle, the difference in states between an impurity at the surface versus an impurity in the bulk can be determined. If metal remains on the surface, as suggested by the copper data, the surface copper can be removed. This removal was verified using synchrotron TXRF, XPS, and TOF-SIMS.

11:00am **AS-FrM9 A Comparative Evaluation of FIB CVD Processes***,* ***B.I. Prenitzer****, B.W. Kempshall, L.A. Giannuzzi,* University of Central Florida*; S.X. Da,* FEI Company*; F.A. Stevie,* Cirent Semiconductor (Lucent Technologies)

The metal chemical vapor deposition (CVD) capability available in focused ion beam (FIB) instruments has found multiple applications, e.g., in semiconductor device modification, for mask repair, and as a means to protect the region of interest during specimen preparation for electron microscopy. Added versatility has been afforded to CVD processes by the introduction of the dual beam FIBs. Dual beam instruments incorporate both an electron column and an ion column into a single FIB, and therefore allow the CVD process to be either ion or electron assisted. Evidence indicates that the mode of deposition may be significant in determining the final properties of the metal line, i.e., chemical composition and resistivity. In addition to the characteristics of the metal line itself, damage has been observed in the surface layers of specimens in which ion beam assisted CVD processes have been employed. Maintaining the integrity of the surface layers is particularly critical when preparing specimens for subsequent microstructural and/or microanalytical evaluation of ultra-shallow regions. Cross-section transmission electron microscopy (TEM) is used to evaluate the surface integrity of single crystal Si substrates on which Pt metal lines have been grown by ion and electron beam assisted CVD processes. The effectiveness of various surface coatings in the prevention of radiation damage during ion beam induced CVD is also investigated.

11:20am **AS-FrM10 High Resolution Sum Frequency Generation of a Rubbed Octadecyltriethoxysilane Self Assembled Monolayer on Glass***,* ***T.E. Furtak****, B.C. Chow,* Colorado School of Mines

Over the last decade, optical sum-frequency generation(SFG) has made the acquisition of vibrational spectra of surface species possible. However, the SFG instrumentation that has usually been employed suffers from low spectral resolution due to the use of band-width-limited picosecond lasers. Using a nanosecond source, we have been able to achieve a resolution nearly two orders of magnitude better than that characterized by a picosecond source. Exploiting this advantage we have observed previously unresolved features in the vibrational spectra of rubbed self-assembled monolayers of octadecyltriethoxysilane(OTE) on glass. We have been able to establish a relationship between the effect which rubbing produces and the surface coverage of the molecule through the ratio of the chain -CH@sub 2@- and terminal -CH@sub 3@ features in the spectrum. This new insight will be of value to surface modification technologies, particularly those involving liquid crystal displays.

11:40am **AS-FrM11 The Use of Field Ionization Methods to Probe the Influence of High Interfacial Electric Fields on Electrochemical Phenomena***,* ***V.K. Medvedev****,* University of Washington*; D.L. Scovell,* University of Washington, U.S.A*; C.J. Rothfuss, E.M. Stuve,* University of Washington

One characteristic of the electrode/electrolyte interface is the presence of high electric fields, typically on the order of 1 V/Å. With sharp field emitter tips, sufficiently high electric fields can be generated at the tip surface by application of a few kV bias potential. We have developed a field ionization microscopy and mass spectroscopy system for studying the influence of high electric fields on ionization of water. Water is adsorbed on a platinum field emitter □adius 350 Å under both field-free and applied field conditions. Water adlayers ranging in thickness from 0 to 5000 Å have been examined at temperatures ranging from 30-300 K at pressures below 10@super -6@ torr. Water ionization was detected by time-of-flight and Wien filter (ExB) mass spectroscopies and imaged on a phosphor screen. Experimental and numerical results to date show that: (1) fields of only 0.2-0.5 V/Å can increase the ionic content of the water layer by several orders of magnitude; (2) the ions formed are hydrated by as many as 10 water molecules; (3) the onset of water ionization on a clean Pt tip increases linearly with temperature over the range of 170-300 K; and (4) ions formed at the tip/water interface must diffuse through the water layer prior to detection. The distribution (n) of (H@sub 2@O)@sub n@H@super +@ clusters is a strong function of ionization conditions and provides information on the nature of surface diffusion as a function of temperature. The diffusional barrier for ion transport through the water layer appears to be a function of applied electric field and the nature (amorphous vs. crystalline) of the water layer.

Biomaterial Interfaces Group
Room 613/614 - Session BI-FrM
Interface, Properties, and Modification

Moderator: B.D. Ratner, University of Washington

8:20am **BI-FrM1 Topographical Polymorphism of a Phospholipid Monolayer***,* ***W.R. Schief****, L.A. Touryan,* University of Washington*; S.B. Hall,* Oregon Health Sciences University*; V. Vogel,* University of Washington

Light scattering microscopy reveals previously undetected topographical complexity in lipid monolayers at the air/water interface. At a surface pressure (@pi@) of @pi@ = 13 mN/m at room temperature, following completion of the liquid-expanded (LE) -> liqu id-condensed (LC) transition, the LC phase of Dipalmitoylphosphatidylcholine (DPPC) develops corrugations within a region covering half the monolayer and surrounding flat, chiral-shaped domains. The scattered intensities of the domains and the surrounding region are analyzed in light of capillary wave theory. With compression over @pi@ = 20 mN/m, the corrugated region becomes decorated with nanoparticles through a reversible budding process. Beyond a threshold of @pi@ = 60 mN/m, the budding accelerates. A tomic force microscopy (AFM) on samples transferred to mica confirms the presence of multibilayer discs of diameter 15 - 150 nm. These findings provide new information on potential surface mechanisms of respiration, since a monolayer enriched in DPPC is widely thought to coat the lung.

8:40am **BI-FrM2 Plasma Co-polymer Surfaces for the Controlled Adsorption of Common Proteins***,* ***J.D. Whittle****, R.D. Short, C.W.I. Douglas,* University of Sheffield, UK*; J. Davies,* Johnson and Johnson Orthoclinical Diagnostics, UK

The topic of protein adsorption is of key interest in biomaterials science, since it is generally believed that subsequent surface reactions are guided by the composition of adsorbed proteins. This is especially pertinent in immunodiagnostics, where nonspecific and poorly characterised protein binding may lead to false positives and poor signal-noise ratios. We are interested in controlling the passive adsorption of several common proteins from single solutions through the molecular engineering of surfaces by means of plasma. We utilise continuous wave rf plasma copolymerisation to allow us to synthesise ultra-thin plasma polymer (PP) films of controllable surface chemistry, from various starting 'monomers'. The plasma polymers are analysed by XPS to allow us to estimate the proportion of different functional groups present in the deposited surface. In this experiment we examine surfaces deposited from plasmas of allyl alcohol and acrylic acid. A range of surface functionalities was produced by copolymerising the functional monomer with 1,7-octadiene. Protein adsorption was estimated by an Enzyme Immunoassay (EIA) after exposing the surfaces to single solutions of human albumin, fibrinogen, vitronectin and IgG overnight at a temperature of 37°C and a pH of 7.0. Results show that the amount of protein adsorbed depends not only upon the protein being investigated, but also the characteristics of the polymer surface, with a clear correlation between functional group concentration and the adsorption of fibrinogen, vitronectin and IgG. The adsorption of albumin is not affected by the funtionality of the surface, however this may reflect a limitation in the technique. SPR measurements suggest that even at low concentrations albumin can form a multilayer on these plasma deposited surfaces, which would lead to poor sensitivity of the assay.

9:00am **BI-FrM3 Reversible Immobilization of a Thermally-Responsive Fusion Protein on a Hydrophobic Surface***, **W. Frey**, N.A. Hattangadi, D.E. Meyer, A. Chilkoti,* Duke University

Elastin-like polypeptides (ELPs), which are composed of repeats of the Val-Pro-Gly-X-Gly (X is a variable residue) pentapeptide, undergo a phase transition as a function of temperature. ELPs are soluble in water below their transition temperature, and are insoluble in water and aggregate when the temperature is raised above the transition temperature. We have synthesized a thioredoxin-ELP fusion protein (Trx-ELP), and shown by ellipsometry, surface plasmon resonance spectroscopy, and atomic force microscopy that below its transition temperature, soluble Trx-ELP does not interact with a hydrophobic surface. However, above the transition temperature, insoluble Trx-ELP forms an adsorbed monolayer on a hydrophobic surface, in which Trx is oriented towards the bulk. Adsorbed Trx-ELP binds an anti-thioredoxin monoclonal antibody with high affinity from solution. The Trx-ELP/antibody complex can be resolubilized from the surface by reducing the solution temperature below the transition temperature. The adsorption transition is driven exclusively by the hydrophobic surface, because no adsorption is observed on a hydrophilic surface, and previously aggregated Trx-ELP in solution does not adsorb onto a hydrophobic surface. The adsorbed Trx-ELP complex shows micelle-like organization, with a mean diameter of approximately 100 nm. Current studies on reversible self-organization of ELP fusion proteins onto micro and nano-patterned surfaces, based on an easily controllable solution parameter, suggest their application in biosensor development and modulation of cell-substrate interactions.

9:20am **BI-FrM4 The Fibronectin Type III Domain: A Scaffold for a Molecular Recognition Switch***, **A. Krammer**,* University of Washington*; H. Lu, B. Isralewitz, K. Schulten,* University of Illinois, Urbana-Champaign*; V. Vogel,* University of Washington

The forced unfolding of fibronectin's tenth type III module (FnIII10) was simulated by steered molecular dynamics (SMD) indicating that mechanical tension applied to the module's termini renders its RGD loop inaccessible to cell surface integrins. FnIII10 possesses a beta-sandwich motif consisting of seven beta-strands (A-G) that are arranged in two antiparallel sheets with the RGD peptide sequence located at the apex of the FG loop. Computer simulations now reveal that the b-strand G separates from the module at an early stage of unfolding while the remaining fold experiences only small structural perturbations. Consequently, the RGD peptide is pulled closer to the module's surface as the FG loop unravels. A molecular scale picture of the forced unfolding pathway will be discussed as well as its implications for the understanding of cell-surface interactions.

9:40am **BI-FrM5 Utilizing Direct Communication between Enzymes and Conducting Polymers in Glucose Sensors***, **A. Kros**,* University of Nijmegen, The Netherlands*; S.W.F.M. van Hövell,* TNO Nutrition and Food Research Institute, The Netherlands*; D.M. Vriezema, R.J.M. Nolte,* University of Nijmegen, The Netherlands

Biosensors are currently of great interest because of the potential to measure a variety of substrates like glucose and lactate.@footnote 1@ Glucose is by far the most studied analyte in this field of research, primarely due to its importance in human metabolic processes. Here we report the development of a glucose sensor, which will be utilized to measure in vivo glucose levels in the near future. The working mechanism of the sensor is based upon direct electron communication between the enzyme glucose oxidase and a conducting polymer.@footnote 2@ In this new glucose sensor, ethylenedioxythiophene is polymerized chemically inside the pores of a cyclopore track-etch membrane using iron(III)chloride as a catalyst. In this way, a thin layer of conducting polymer (polyethylenedioxythiophene, pedot) is deposited in the interior of the pores. The latter layer is subsequently covered with the redox enzyme glucose oxidase by means of physical adsorption and electrostatic interactions between the positively charged pedot and the negatively charged enzyme. The resulting sensor is able to detect glucose in the clinical relevant concentration range via amperometric methods. The influence of electrostatic interactions and the use of electronic mediators on the sensor performance will be discussed. @FootnoteText@ @footnote 1@ A.E.G. Cass, A practical approach, Oxford University Press, New York, 1994. @footnote 2@ C.G.J. Koopal, B. de Ruiter, R.J.M. Nolte, J. Chem. Soc. Chem. Commun., 1991, 1691.

10:00am **BI-FrM6 Cap-shaped Gold Nano Particles for Optical Biosensing***, **M. Himmelhaus**, H. Takei,* Hitachi, Ltd., Japan

Gold nano particles can be utilized for optical detection of biomolecules.@footnote 1, 2@ The approach presented here is well suited for the development of miniaturized, inexpensive biosensors for two reasons. First, the preparation of the sensing surface is easy to control and highly reproducible. Second, the unique optical properties of cap-shaped gold particles, such as a pronounced reflectivity minimum in the visible region of OD. 2.4 with a bandwidth of 100 nm, lead to a highly sensitive though simple optical read-out quantity. For preparation, a gold layer of 20 nm is first evaporated on a polystyrene (PS) substrate. Then, the gold layer is exposed to an aqueous PS nano sphere suspension containing a small amount of carbodiimide. Addition of the last chemical to the commercially available monodisperse PS sphere suspension leads to formation of a dense monolayer of randomly positioned PS nano spheres on the gold thin film. After one hour of incubation, superfluous PS spheres are simply washed off with deionized water. Finally, a gold layer of 20 nm thickness is evaporated onto the PS sphere monolayer leading to formation of cap-shaped gold particles. The resulting surface exhibits a pronounced extinction peak upon reflection of visible light. The shift of this reflectivity minimum due to changes in the refractive index of the immediate environment can be monitored with simplest optical methods and therefore is well adapted to miniaturization. We will show that a straightforward fiber-optical setup is sensitive enough to detect in-situ monolayer formation of alkanethiolates. Further, the capability of sensing biomolecular adsorption will be demonstrated utilizing the biotin/avidin functional pair as a model system. @FootnoteText@ @footnote 1@R. Elghanian, J. J. Storhoff, R. C. Mucic, R. L. Letsinger and C. A. Mirkin, Science 277 (1997) 1078-81 @footnote 2@F. Meriaudeau, T. R. Downey, A. Passian, A. Wig and T. L. Ferrell, Appl. Opt. 37 (1998) 8030-7.

10:20am **BI-FrM7 Properties of Thiol Monolayers in Contact with Liquids: An In Situ Investigation by IR-vis Sum Frequency Spectroscopy***, **M. Zolk**, F. Eisert, M. Buck, M. Grunze,* University of Heidelberg, Germany

In the vast majority of cases the analysis of the structure and properties of self-assembled monolayers (SAM) takes place ex situ, e.g. in air or even under vacuum. In contrast, the application in fields relevant to biotechnology requires a detailed understanding of their properties in contact with liquids, in particular aqueous solutions. This raises the question of the relevance of ex situ investigations to conditions relevant for applications. We report experiments on SAMs of thiols on gold and metal substrates. The behavior of pure and end group modified thiols in contact with different liquids is studied. In particular, we focus on SAMs which consist of a methoxy terminated ethylene glycol (EG) unit attached to an alkane thiol. Whereas SAMs of pure alkane thiols are affected relatively little by solvents, EG-SAMs which are important for the preparation of protein resistant surfaces, exhibit a drastic dependence on the environment. All solvents examined penetrate the layer and induce significant conformational changes. Compared to air the signal from the methoxy end group is strongly reduced in contact with solvents. This indicates a transition from a well-ordered to an amorphous state. Analogously, the methylene vibrations gain intensity and thus indicate an increase of gauche conformations. Depending on the solvent the degree of penetration is different. A polar solvent such as water mainly interacts with the EG part of the layer whereas non-polar solvents interact as well with the hydrocarbon chain and thus penetrate deeper into the SAM. The experiments clearly demonstrate the need to investigate SAMs under conditions relevant for applications.

10:40am **BI-FrM8 Biofilm - Titanium Chemistry of Adhesion Using X-ray Photoelectron Spectroscopy**, ***R.A. Brizzolara***, NSWC - Carderock Division

Virtually all surfaces immersed in water for any period of time are colonized by microorganisms. These organisms adhere to the surface by producing extracellular polymers, predominantly polysaccharides. Biofilm formation and resulting biofouling cause serious problems for heat transfer equipment due to inhibited water flow and degradation of the heat transfer coefficient. Conventional coatings cannot be applied to heat transfer materials due to degradation of the heat transfer coefficient. Titanium, often the material of choice for heat transfer applications because of its corrosion resistance, is very prone to biofouling. Materials and/or surface modification strategies to decrease the strength of adhesion or the rate of biofilm formation would be of great value. As a first step in developing such a strategy, the interfacial chemistry between biofilm components and titanium is being investigated. This paper reports on the use of x-ray photoelectron spectroscopy to examine the interfacial chemistry between alginic acid and n-acetyl glucosamine and titanium. XPS is used to quantify the adsorbate bound to the surface under various conditions (including pH and salt content of the water), and to evaluate the adsorbate-surface bonding mechanism. Information regarding the biofilm-surface chemical interaction will be useful in developing better fouling resistant surfaces. The NSWC Carderock Division In-House Laboratory Independent Research Program supported this work.

11:00am **BI-FrM9 Planar Polymerized Phospholipid Bilayers as Biocompatible Substrates**, ***J.C. Conboy***, *S. Liu, D.F. O'Brien, S.S. Saavedra,* University of Arizona

There is considerable interest in finding a surface that is resistant toward non-specific protein adsorption and is chemically and mechanically stable. Hydrophilic surfaces, such as those of a zwitterionic phospholipid bilayer, are inherently biocompatible with intrinsically low nonspecific protein interactions. However, planar supported lipid bilayers are only weakly associated, making their stability less then desirable from an applications standpoint. Toward the goal of producing a stable and intrinsically biocompatible substrate, we endeavored to produce planar polymerized analogs of phospholipid bilayers. A photosensitization method was used to polymerize the lipid bilayers in aqueous media. The rate of polymerization and subsequent structural changes in the lipid film were examined by in-situ Raman spectroscopy. The stability of the lipid films was determined before and after in-situ polymerization by a number of methods. Their application as substrates for optical biosensors will also be discussed.

11:20am **BI-FrM10 Nanoscale Patterning of Gold for Attachment of Supported Lipid Bilayers**, ***A.T.A. Jenkins,*** Max-Planck Institut für Polymerforschung, Germany

Attaching lipid bilayers to solid substrates in such a way that they exhibit properties analagous to cell membranes found in Nature is becoming of increasing interest. Such systems have the potential to be used as biosensors and for fundamental studies of cell membranes. In this paper we present a novel method of attaching such lipid bilayers to gold substrates using microcontact printing to produce a patterned surface of sub-micron size patterns onto which a lipid layer is added. Microcontact printing has been used to form patterns of lipophilic Self-assembled monolayers (SAMs) on gold with dimensions of 500 nm or less. These patterns consist of a regular array of hydrophilic and hydrophobic patches. Onto these patterned SAMs, lipid bilayers have been formed over the hydrophilic patches by lipid vesicle rupture and self-assembly. Investigation of lipid bilayers on these small nanometer scale patterns compared with larger micrometer scale patterns of lipopilic SAMs, by both Impedance Spectroscopy and Surface Plasmon Spectroscopy have suggested that vesicle adsorption followed by rupture at hydrophilic-hydrophobic SAM interfaces may be a crucial part of the mechanism of bilayer formation on such patterned SAMs. Finally, ion-selective peptides and proteins including Valinomycin and Gramicidin have been inserted into the bilayer patches, and the expected ion-selectivity observed experimentally.

Electronic Materials and Processing Division
Room 608 - Session EM-FrM

In Situ Monitoring and Growth

Moderator: C.R. Abernathy, University of Florida

8:20am **EM-FrM1 Optical Techniques for Real-Time Measurement of Stress and Morphology During Thin Film Growth**, ***J.A. Floro,*** Sandia National Laboratories **INVITED**

Mechanisms for the generation and relaxation of stresses in thin films during deposition have been subject to extensive scientific research and technological tweaking. Stress evolution during film growth can be quite complex, and is best measured in real-time during the deposition process. The primary focus of this talk will be on the use of substrate curvature measurements, since this approach has the greatest degree of flexibility in its implementation. The use, limitations, and extensions of the Stoney equation, which relates substrate curvature to film stress, will be discussed. Methods for curvature measurement will be surveyed, with emphasis on a recently developed laser-deflection technique that is currently being applied to a wide range of thin film systems. I will present several instructive examples on the interpretation of real-time stress data obtained during the deposition of heteroepitaxial and polycrystalline thin films. Finally, a new spectroscopic light scattering technique will be introduced that provides real-time measurement of surface morphological evolution. 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.

9:00am **EM-FrM3 Insitu Surface Stress Measurements during Contact Reaction of Ultrathin Overlayers of Cobalt on Si(100) and Si(111)**, ***J.G. Nivison***, *D.G. Waters, P.A. Bennett,* Arizona State University

We report insitu measurements of surface stress during the contact reaction of 10 Angstrom overlayers of cobalt on Si(111) and Si(100) using an optical deflection wafer curvature technique. The instrument features a feedback stabilized reference beam, which removes thermal drift to first order, allowing temperature dependent measurements. For Si(100), the surface stress during room temperature dosing is +0.2 N/m per Ml (tensile), saturating at 8Ml. Upon annealing, the stress increases monotonically to +0.6 N/m at 200C, which is attributed to a partially coherent CoSi2 overlayer. For Si(111), the stress during room temperature dosing is +0.6 N/m for the first Ml, changing to -4.5 N/m at 5Ml coverage. Upon annealing, the stress increases to +4.0 N/m at 450C, which is attributed to a fully coherent CoSi2 overlayer.

9:20am **EM-FrM4 Vibration Analysis of SiH@sub n@ Bending Modes on Hydrogenated Si(100) Surface Using Infrared Reflection Absorption Spectroscopy**, ***H. Noda***, *T. Urisu,* Institute for Molecular Science, Japan*; M. Hiramatsu,* Meijo University, Japan

Detailed analyses have been successfully made for the SiH@sub n@ stretching vibration mode on hydrogenated Si(100) surface, which is of great scientific and technological interest.@footnote1@ However, concerning the bending vibration region, which gives important information about SiH@sub 2@ and SiH@sub 3@ species, very little work has been done. Recent developments of buried metal layer infrared reflection absorption spectroscopy (BML-IRRAS) have made the high-resolution vibration analysis of bending region easy. In this work, adsorption and desorption of hydrogen on Si(100) surfaces have been investigated by measuring BML-IRRAS covering a wide spectral range (800-2200 cm@super-1@). In both 3x1 and 1x1 phases observed with reflection high-energy electron diffraction (RHEED), a doublet peak (902 and 913 cm@super -1@) has been clearly observed and assigned to the SiH@sub 2@ scissors mode. The splitting of the peak is most likely due to the frequency difference of SiH@sub 2@ scissors vibration between single SiH@sub 2@ (ordered 3x1 units ; H-Si-Si-H H-Si-H H-Si-Si-H) and neighboring SiH@sub 2@ (disordered 3x1 units ; H-Si-Si-H H-Si-H H-Si-H H-Si-Si-H). Coverage and annealing temperature dependence of this doublet peak have also been investigated. @FootnoteText@ @footnote 1@ Y. J. Chabal and K. Raghavachari, Phys. Rev. Lett. 54 (1985) 1055.

9:40am **EM-FrM5 Assessment of Various Sensors for in-situ Monitoring and Control of MBE**, ***K.G. Eyink***, Air Force Research Laboratory

Molecular Beam Epitaxy is a technique, which has been used to grow semiconductor thin film structures. In this process reactants fluxes are incident onto a substrate held at an elevated temperature. Typically the structure is grown by an appropriate shuttering sequence that is based on extensive pre-calibration. In this talk I am going to discuss the use of several sensors to monitor MBE in real-time. A discussion of the advantages and disadvantages of the various techniques will be given. The utilities of ellipsometry, desorption mass spectrometry, and atomic absorption for in-situ targeting of composition and growth rates will be given. As well as the advantage of integrating absorption band edge spectroscopy into substrate temperature control and its coupling to the various other sensors.

10:00am **EM-FrM6 Integrated Real-time SE, RDS and QMS to Characterize and Optimize OMCVD Growth***, **K.A. Bell**, M. Ebert, S.D. Yoo, K. Flock, D.E. Aspnes,* North Carolina State University

We combine spectroscopic ellipsometry (SE) and reflectance-difference spectroscopy (RDS) in a single optical path with quadrupole mass spectrometry (QMS) on an OMCVD reactor to probe bulk and surface properties as well as ambient composition in real time during growth. This unique system enables us to characterize the complex parameter space of OMCVD and optimize growth conditions. Monitoring the optical response of the sample and gas phase species enables us to determine ideal growth parameters for our reactor and to characterize growth mechanisms. The optical spectrometer is a multichannel, parallel acquisition and processing system built around a commercial rotating-spindle OMCVD reactor and a custom photodiode array (PDA) detector that allows us to extract sample optical properties over a spectral range of 200 to 800 nm at a repetition rate of 2 Hz. Together with time-resolved QMS, we determine system-specific parameters necessary to calibrate temperature and characterize gas flow dynamics. The former has been done using reciprocal space analysis of SE data to extract sample critical point energies in real time with an accuracy of 0.5 meV corresponding to +/-1 degree in sample temperature. Monitoring the growth of GaP on Si(001) in real time, we observe a SE sensitivity to 0.1 Angstrom changes in thickness and a QMS sensitivity of 0.1% changes in ambient composition.

10:20am **EM-FrM7 Real-time Thickness and Compositional Control of Ga1-xInxP Growth using P-Polarized Reflectance***, **V. Woods**, K. Ito, I. Lauko, N. Dietz,* North Carolina State University

Advances in the engineering and design of advanced electro-optical materials require sensors and control strategies that allow tight control over thickness and composition. In response to this demand, we developed p-polarized reflectance (PR) as a real time optical characterization technique, and demonstrate its sensitivity during heteroepitaxial GaP/GaInP growth under pulsed chemical beam epitaxy (PCBE) conditions. For closed loop control, we applied nonlinear control algorithms (based on nonlinear Kalman filtering) that utilizes the PR signals to control thickness and composition during heteroepitaxial growth of GaxIn1-xP on Si (001). A reduced order surface kinetics (ROSK) model has been formulated to describe the decomposition process of organometallic precursors and the time-dependency of the molar concentrations of the precursors fragments. These data are linked to compute the composition and thickness increase per time unit, utilizing the monitored PR signal for validation. This allows to establish feedback control algorithms, able to control both the growth rate and composition of GaxIn1-xP heterostructures.

10:40am **EM-FrM8 Migration-Enhanced Epitaxy of CuInSe@sub 2@***, **B.J. Stanbery**, S. Kincal, S. Kim, O.D. Crisalle, T.J. Anderson,* University of Florida

We describe a novel rotating-disc MBE reactor that implements a Migration-Enhanced Epitaxy (MEE) process@footnote 1@ and its application to the growth of Copper Indium Selenide (CIS) on GaAs and ZnTe single-crystal substrates. MEE is a process variant of conventional MBE and one of a general class of Modulated-Flux Deposition (MFD) processes that are based on cyclic alternation between deposition and relaxation steps, and the separation of cationic and anionic species fluxes. All of these measures are intended to achieve long surface diffusion lengths and promote adatom/substrate equilibration. Our reactor is divided by carefully designed shielding into four nominally isolated zones: metals (Cu+In) deposition, cooling, chalcogen (Se,S) deposition and heating. The fixed substrate heater in the latter zone combined with the rotating-disc design results in cyclic heating and cooling of the substrates. The direction of substrate rotation can be reversed, enabling two different growth cycles. The cooling zone includes a source for dosing the substrates with dopants or surfactants. We will present the results of our molecular and thermal flux modeling and discuss their implications for surface growth kinetics in our reactor. We will also present XRD, AFM, Auger, SIMS and PL data characterizing our successful epitaxial growth by MEE of (001)CuInSe@sub 2@ on (001)GaAs and (001)ZnTe. Our data also shows phase segregation of Cu@sub 2-X@Se in copper-rich epilayers and a relative loss of crystal quality in indium-rich epilayers. We will discuss the relevance of these results to our free-energy thermochemical defect model of the Cu-In-Se ternary system. We show that these data provide evidence of a transition from Stranski-Krastonov to Frank-Van de Merwe growth mode when the surface is dosed with small quantities of sodium fluoride during the initial stages of epitaxy on (001)ZnTe, supporting our thesis@footnote 2@ that sodium behaves as a surfactant in this material system. @FootnoteText@ @footnote 1@ Y. Horikoshi, M. Kawashima, and Y. Yamahuchi, Jap. J. Appl. Phys. 25, 1986, p. L868. @footnote 2@ B.J. Stanbery, C.-H. Chang, and T.J. Anderson, 11th International Conference on Ternary and Multinary Compounds, 1997, Inst. of Phys. Conf. Series 152, pp. 915-922.

11:00am **EM-FrM9 Boron Nitride Thin Films for High Temperature Multilayer Ceramic Capacitor Chips (MLC3's)***, **N. Badi**, D. Starikov, N. Medelci, I.E. Berishev, A. Bensaoula,* University of Houston

There is a great need for miniaturized, high power density, low cost capacitors that operate at high frequency and can sustain high operating temperatures. In our laboratory we are investigating the use of boron nitride (BN) based materials for such devices. Advantages of BN include high temperature and chemical resistance which should result in more compact, and reliable devices. We investigate here, the temperature stability of different multilayer capacitor heterostructures (e.g. TiN/BN/TiN/Si, Cu/BN/Cu/quartz, Cu/AlN/Si). To study the interdiffusion between the dielectric and the electrodes at elevated temperatures, we performed secondary ions mass spectroscopy (SIMS) on two structures: (I) TiN/B/BN/Si and (II) B/TiN/Si. In this manner we minimize ion mixing effects in determining the quality of the relevant interfaces (TiN/B/BN and B/TiN/Si) at annealing temperatures up to 500 °C. High resolution SEM pictures from TiN/BN/TiN/Si samples showed dense boron nitride layers with sharp interfaces. However Cu/AlN/Si structures showed copper diffusion into the silicon substrate due to the columnar structure of the single crystal AlN films. I-V measurements revealed the highly insulating properties of TiN/BN/TiN/Si capacitor. In fact a breakdown voltage (BDV) of 400 V/mm was measured for a 2000 Å BN thin layer. C-V measurements from a 3mm x 4 mm planar structure, show a capacitance value of 1.1 nF at 10 KHz and 1 Vrms. Furthermore the temperature dependence of C-V characteristics, dissipation factor, insulation resistance, and reliability of the ceramic capacitor will be presented. This work was supported by funds from a NASA cooperative agreement #NCC8-127 to SVEC, a Texas Advanced Technology Program Grant # 1-1-32061, and the Ballistic Missile Defense Organization/Science and technology and managed by William Shoup from The DTRA/CPTI. @FootnoteText@ *A. Bensaoula email address: Bens@jetson.uh.edu.

11:20am **EM-FrM10 The Deposition of Polycrystalline Si and SiGe by Ultra-high Vacuum Chemical Vapor Deposition System***, **K.M. Chen**, H.J. Huang,* National Chiao Tung University, Taiwan, R.O.C.*; L.P. Chen, G.W. Huang,* National Nano Device Laboratory, Taiwan, R.O.C.*; C.Y. Chang,* National Chiao Tung University, Taiwan, R.O.C.

The polycrystalline Si@sub 1-x@Ge@sub x@ (poly-Si@sub 1-x@Ge@sub x@) films have better properties than poly-Si for device fabrications, such as lower transition temperature and process thermal budget. For these reasons, the poly-Si@sub 1-x@Ge@sub x@ films have been utilized for low-temperature TFT fabrications and gate electrodes of MOS transistors. In this work, disilane and germane were used to grow poly-Si@sub 1-x@Ge@sub x@ films at low temperature (0.1). This implies that the growth mechanism of poly-Si@sub 1-x@Ge@sub x@ films is different from that of epitaxial Si@sub 1-x@Ge@sub x@ on Si. The uniformity of poly-Si@sub 1-x@Ge@sub x@ films depends on the Ge content, and it is improved by the addition of germanium. The result can be explained by the lower activation energy (< 0.25 eV) related to deposition of poly-Si@sub 1-x@Ge@sub x@, as compared to that of poly-Si (~2.1eV) in the surface-reaction limited growth mode. From the XRD and AFM analyses, the crystallinity and roughness of films are suitable to device fabrications.

Magnetic Interfaces and Nanostructures Technical Group
Room 618/619 - Session MI-FrM

Magnetic Thin Films

Moderator: C.J. Palmstrom, University of Minnesota

8:20am **MI-FrM1 New Phenomena in Laterally Modulated Magnetic Thin Films***, **Z.Q. Qiu**,* University of California, Berkeley **INVITED**

Ultrathin magnetic films grown on atomically stepped surfaces exhibit many interesting properties due to the lateral modulation at the nanometer scale. To systematically control the atomic steps curved substrates are utilized to provide a continuous range of step density. Fe and Co films grown on curved Ag(001), W(001) and Cu(001) have been investigated by means of the surface magneto-optic Kerr effect. The atomic steps induce an in-plane, uniaxial magnetic anisotropy with the easy axis either parallel or perpendicular to the step edges. The strength of the step-induced anisotropy is linearly roportional to step density for fcc magnetic films, but scales quadratically for bcc magnetic films. The Neel pair-bonding model provides a possible explanation for these observations. Even more intriguing results occur when substrate magnetism is induced at the stepped interface, as for the Fe/Pd(001) system. The ferromagnetic nature of the interfacial fcc Pd dominates the anisotropy to result in a linear dependence of the step-induced anisotropy on step density even though the Fe overlayer is bcc. The step-induced moment in this system is also shown to enhance the Curie temperature. Finally, for the Fe/Cr(001) system, the compensated, stepped Cr(001) surface is found to produce a 90-degree coupling between the Fe and Cr moments. When this effect competes with the step-induced anisotropy, the Fe magnetization undergoes an in-plane spin-reorientation transition from perpendicular to parallel to the step edges with increasing step density.

9:00am **MI-FrM3 Interrelation of Morphology and Structure in Ultrathin Magnetic fcc FeCo Alloy Films on Cu(001)**, ***W. Kuch***, *A. Dittschar,* Max-Planck-Institut für Mikrostrukturphysik, Germany; *M. Zharnikov,* Universität Heidelberg, Germany; *C.M. Schneider,* Institut für Festkörper- und Werkstofforschung Dresden, Germany

Chemically random epitaxial ultrathin alloy films allow the study of correlation between morphology, structure, and magnetism for continuously varying structural parameters. This can be achieved if variation of the film composition leads to a continuous alteration of film properties such as the lattice constant and the average magnetic moment. We present a multi-technique investigation of structure, morphology, and magnetism of epitaxial Fe@sub x@Co@sub 1-x@ alloy ultrathin films grown on Cu(001) over the whole composition range up to thicknesses of 9 ML. The films grow at room temperature in a distorted fcc structure with random chemical order. The amount and sign of the distortion depend on thickness and composition. Below 60-70% Fe content the alloy films are smooth and tetragonally compressed in the vertical direction in the interior of the films, with tetragonally expanded layers at the surface. The strain is continuously reduced with increasing Fe concentration, and at 60-70% Fe content the interior of the films reaches the unstrained fcc structure. For higher Fe concentrations the occurrence of several superstructures is observed, which are attributed to regular structural rearrangements. At the same time the roughness of films with more than 4-6 ML is significantly enhanced. This is discussed in terms of the vertical strain at Fe concentrations above 70%, the sign of which is reversed with respect to lower Fe concentrations, leading to tetragonally expanded layers. No indications for the presence of low-moment fcc Fe were found in any of the films.

9:20am **MI-FrM4 Structure and Magnetic Properties of Cu/Co/Cu/H-Si(110) Films**, ***S. Maat***, *M.T. Umlor, G.J. Mankey,* University of Alabama

We report the results of a study of the structural and magnetic properties of Co films deposited on Cu/H-Si(110). A Cu(111) buffer layer is formed by evaporation or UHV sputter deposition on the H-terminated Si(110) surface. From consideration of bulk lattice constants, the Cu films undergo a 6% expansion along the [1, -1, 0] direction and a 13% compression along the [1, 1, -2] direction. The structure as a function of buffer layer thickness from 1 nm to 100 nm is determined with a combination of LEED, Auger electron spectroscopy and RHEED. The optimum sputtering conditions for producing well-ordered fcc(111) films were determined. The buffer layer crystallography was found to be strongly dependent on the sputtering conditions, with a transition from polycrystalline to single-crystal as the sputtering power is increased. Evaporated films were found to grow as single crystals. Co films grown on single-crystal buffer layers exhibit a six-fold LEED pattern with diffuse spots. The Co films were capped with a protective Cu layer and the magnetic properties were measured ex-situ with MOKE and MFM. MOKE data perpendicular to the Cu [1, -1, 0] direction reveals a stepped hysteresis loop shape characteristic of a combination of triaxial and uniaxial in-plane anisotropy. This loop shape is attributed to a combination of uniaxial strain incorporated in the films and the three-fold crystalline anisotropy of the hcp structure. @FootnoteText@ Supported by DOD grant DAAH04-96-1-0316 and shared equipment through NSF grant DMR-9809423.

9:40am **MI-FrM5 Magnetization Reversal in Ultrashort Magnetic Field Pulses**, ***H.C. Siegmann***, *C.H. Back,* Swiss Federal Institute of Technology, Switzerland; *R. Allenspach,* IBM Zurich Research Laboratory, Switzerland **INVITED**

Ultrashort magnetic field pulses with amplitudes of up to 20 Tesla at picosecond duration are generated in the final focus test beam facility of the Stanford Linear Accelerator. These unique magnetic field pulses have been used to study magnetization reversal in a variety of thin ferromagnetic films. High resolution magnetic contrast images reveal the magnetization patterns generated by one or several field pulses from which we deduce the elementary processes responsible for the magnetization reversal. For perpendicular magnetized samples we observe ring domains which are reminiscent of the field contour lines during exposure. Their radii represent switching fields which are in quantitative agreement with the coherent rotation model. The broadening of the transition region between oppositely magnetized domains is due to static and dynamic fluctuations of the magnetic anisotropy. For films with uniaxial anisotropy in the plane of the film we observe "figure 8" magnetic patterns due to the necessity to conserve angular momentum while generally much smaller fields compared to the perpendicular samples are sufficient for the ultrafast reversal. We show that the demagnetizing field produced by the precession of the magnetization out of the plane of the film completes the reversal after the external field ceases to exist. The material property of primary importance in ultrafast reversal is the damping of the precession of the magnetization around the direction of the external field. We show that it is strongly influenced by the degree of crystallinity of the sample.

10:20am **MI-FrM7 Ginzburg-Landau Theory of Perpendicular Magnetized Ultrathin Films**, ***A. Berger***, Argonne National Laboratory

Ultrathin ferromagnetic films have been found to exhibit a strongly enhanced magnetocrystalline anisotropy, which can even be sufficient to overcome the demagnetizing effect and stabilize a perpendicular magnetized state in the entire ferromagnetic temperature range. Such perpendicular magnetized systems have been particularly interesting with respect their thermodynamic properties and were reported to confirm predictions for the two-dimensional Ising model. However, recent experiments on perpendicular magnetized Ni/Cu(100)-films have shown indications for domain formation near the Curie temperature that seems to occur without weakening of the effective anisotropy (crystalline + dipolar).@footnote 1@ Therefore, this observation seems to be fundamentally different from earlier results reported for a number of ultrathin film systems where domain formation is found in the immediate vicinity of the reorientation phase transition, which is associated with the vanishing of the effective anisotropy. To understand the above phenomena we have evaluated the free energy of a perpendicular magnetized material using the Ginzburg-Landau theory. In accordance with previous results, we find that for sufficiently large anisotropy values no conventional domain structure is formed at any temperature. However, we find that a domain structure based on the formation of linear domain walls (LDW-phase) lowers the energy in a substantial region around the critical point. In addition, the domain size is estimated to be microscopically small so that this domain structure should be formed for any realistic sample size. We will discuss the details of the calculated phase diagram with particular emphasis on the implication that the LDW-phase prohibits a direct ferromagnetic, paramagnetic phase transition. Work supported by the U. S. Department of Energy, Basic Energy Sciences, Materials Science under Contract W-31-109-ENG-38. @FootnoteText@ @footnote 1@P. Poulopoulos et al., Phys. Rev. B 55, 11961 (1997).

10:40am **MI-FrM8 Dimensional Crossover in Ultrathin Ni Films on Cu**, ***R. Zhang***, The Pennsylvania State University; *M. Hochstrasser,* The Pennsylvania State University, U.S.; *N. Gilman, R.F. Willis,* The Pennsylvania State University

Theory predicts that in a magnetic system the long-range order parameter, the magnetization, as a function of the temperature disappears at the Curie temperature according to M=M@sub 0@(1-T/T@sub C@)^@beta@. For 3D Heisenberg and Ising systems @beta@ are 0.365 and 0.325 respectively. For 2D Ising system @beta@ is 0.125. In our experiments, we have studied the finite-size-effect shift of the T@sub C@(n) of a thin film of n layers, as phenomenologically described by the shift exponent @lambda@. There are two ways of defining this exponent. Traditionally, one measures the shift of T@sub C@(n) with respect to the bulk critical temperature T@sub C@(bulk). Alternatively, one may also define: @Delta@T:=[T@sub C@(bulk)-T@sub C@(n)]/T@sub C@(n) ~ n^(-@lambda@'), which defines @lambda@'. We studied with the surface magneto-optical Kerr effect (SMOKE) the behavior of @beta@ and

@lambda@ of Ni films on Cu(100), Cu(110) and Cu(111) in a wide temperature range and with changing thickness. We observe a different behavior for films on Cu(100) and Cu(110) compared to films on Cu(111). Ni films on Cu(100) and Cu(110) show a sharp transition from a 3D Heisenberg @beta@ value to a 2D exponent of ~0.21, whereas for Ni films on Cu(111) no such sharp transition can be observed. This behavior is a strong indication of the role of quantum size effects on the behavior of electronic states, i.e., the sharp transition is a manifestation of quantum-well states existing in a gap in the bulk continuum of sp states, and the absence of such a gap along the direction (E.D. Hansen et al. J.Phys, 9, L435 (1997)). The transition is indicative of a cross-over from 3D to 2D. The finite-size scaling exponents reflect the magnetic behavior of the bulk phase with corrections, as recently argued theoretically by Henkel et al.(PRL, 80, 4783 (1998)). What this work shows is that field theoretic corrections are sensitive to the symmetries of the epitaxial lattices.

11:00am **MI-FrM9 Enhancement of Perpendicular Magnetic Anisotropy and Surface Alloy of Co/Pt(111) Ultrathin Films**, *C.S. Shern, H.Y. Her,* ***Y.E. Wu,*** National Taiwan Normal University, ROC

The magnetic anisotropy of Co/Pt(111) was studied by surface magneto-optic Kerr effect (SMOKE). The perpendicular magnetic anisotropy appears for Co deposited on a flat Pt(111) surface with a thickness between 0.8 and 3.7 ML. The perpendicular uniaxial magnetic anisotropy disappears for Co deposited on a sputtered Pt(111) surface because the magnetocrystalline anisotropy has diminished due to the absence of crystalline structure in the films. During surface alloy formation in 1 ML Co on the flat Pt(111) surface, we quantitatively demonstrate an enhancement in the magneto-optic Kerr signal. The maximum enhancement in MO signal is as large as 200 % after alloy formation at 710 K. The formation of Co-Pt alloy was confirmed by AES and LEED. The perpendicular magnetic anisotropy persists in the annealing process until the ultrathin film is annealed at temperatures above 850 K. The enhancement is also observed in thicker films when the formation of Co-Pt alloy has been developed, but both the out-of-plane and the in-plane anisotropy appear at a higher annealing temperature.

Nanometer-scale Science and Technology Division
Room 611 - Session MS+PS-FrM

Diagnostics and Processes in Etching

Moderator: P.L.G. Ventzek, Motorola Inc.

8:20am **MS+PS-FrM1 Effect of CH@sub 3@F/C@sub 4@F@sub 8@ Ratio on the SiO@sub 2@-to-Si@sub 3@N@sub 4@ Selectivity in a Self-Aligned-Contact Etching Process for Giga-bit DRAM**, ***S.C. Park,*** Hyundai Electronics Industries Co. Ltd., Korea*; J.S. Kim,* Hyundai Electronics Industries Co. Ltd., Korea, South Korea*; J.J. Lee, K.T. Kim, D.D. Lee, Y.S. Seol, I.H. Choi,* Hyundai Electronics Industries Co. Ltd., Korea

Effect of CH@sub 3@F/C@sub 4@F@sub 8@ ratio on the SiO@sub 2@-to-Si@sub 3@N@sub 4@ selectivity in a self-aligned-contact(SAC) oxide etching process was investigated using an inductively coupled plasma. As published in other studies, the SiO@sub 2@-to-Si@sub 3@N@sub 4@ selectivity usually increases as the CH@sub 3@F/C@sub 4@F@sub 8@ ratio increases.@footnote 1@ However, we found out in this work that the selectivity gradually increases to a specific peak and sharply drops as the CH@sub 3@F/C@sub 4@F@sub 8@ ratio continuously increases. Moreover, the selectivity was extremely poor at the valleys between the word lines (and in some cases, the nitride layer was even 'punched through'), while the selectivity was very high at the top shoulder of word line at a certain CH@sub 3@F/C@sub 4@F@sub 8@ ratio. It was found from the XPS and SEM analysis that the fluorocarbon film was built up without any bonding state change, as the CH@sub 3@F/C@sub 4@F@sub 8@ ratio increased. The increase in the selectivity with increasing CH@sub 3@F/C@sub 4@F@sub 8@ ratio should be related with the amount of the fluorocarbon polymer deposition on the surface of Si@sub 3@N@sub 4@ barrier.@footnote 2@ However, the analysis of the fluorocarbon films could not completely explain the sharp drop in the selectivity and the extremely low selectivity at the valley between the word lines. Further studies showed that step coverage of the polymer film formed during the SAC oxide etching was very poor as the contact size decreased and the CH@sub 3@F/C@sub 4@F@sub 8@ ratio increased. In this case, less amount of the fluorocarbon gases should enter the contact hole and less amount of fluorocarbon polymer should be deposited on the Si@sub 3@N@sub 4@ etch barrier. This will eventually result in the sudden drop in the selectivity. @FootnoteText@ @footnote 1@ Y. Iijima and H. Okano, Jpn. J. Appl. Phys, Vol. 36, 5498 (1997) @footnote 2@ N.R. Rueger and G.S. Oehrlein, J. Vac. Sci. Technol. A 15, 1881 (1997

8:40am **MS+PS-FrM2 Plasma Cleaning of Via Bottoms Following Dielectric Etching**, ***P.J. Matsuo,*** *M. Schaepkens, G.S. Oehrlein,* State University of New York at Albany

In plasma etching, aspect ratio effects have been well documented. However,the dependence of the necessary cleaning steps following the etch on feature geometry have not. Cleaning via bottoms following the dielectric etch step can be critical to achieving low resistance contacts in multi-layer metallization schemes. Reducing this resistance is a prerequisite for the proper electrical function of Cu/low-k dielectric wiring architecture. We have examined in-situ surface modifications of post-etch blanket surfaces of several materials (Si, Cu, TiN, Al), resulting from Ar and O@sub 2@ cleaning treatments, using ellipsometry and XPS. We also investigated the removal efficiency of fluorocarbon and oxide residues at via bottoms for realistic aspect ratio structures by measuring the removal rate of fluorocarbon films or oxide films during O@sub 2@ plasma and Ar sputter cleaning, respectively. Ion driven cleaning procedures such as oxide removal, do not show a significant dependence on feature aspect ratio. On blanket films, to vias with an aspect ratio of 3, Ar sputter rates of BPSG remain constant. The removal of fluorocarbon residues under high density O@sub 2@ plasma exposure is heavily dependent on the neutral flux and is reduced in accordance with geometrical shadowing offset by the constant ion component. We have also investigated the surface chemistry of the residues as a function of feature geometry and cleaning process parameters.

9:00am **MS+PS-FrM3 Molecular Dynamics Simulations of Fluorocarbon Films**, ***J. Tanaka,*** Hitachi, Ltd., Japan*; C.F. Abrams, D.B. Graves,* University of California, Berkeley

Fluorocarbon plasma processes are used for highly selective etch processes of SiO@sub 2@ with respect to Si, SiN or photoresist. During fluorocarbon plasma etching, it is known that fluorocarbon films form on the latter surfaces, protecting them from active etch species such as F atoms. Even on actively etched surfaces of SiO@sub 2@, thin fluorocarbon films have been detected. During etching, the fluorocarbon films are an active participant, and in order to optimize etch processes, understanding these films is important. However, the structure and mechanisms of fluorocarbon film formation are not well understood. The nature of fluorocarbon film structure and its role in etching depend on the neutral and ionic species that impact it from the plasma, as well as the underlying material. We have chosen to use molecular dynamics of fluorocarbon ions impacting a carbon surface as a first step in understanding this complex process. In order to use molecular dynamics, we have developed a new C-F intermolecular potential. Our potential was developed based on the reactive empirical bond order (REBO) potential, using a strategy originally developed for carbon-hydrogen interactions. (Brenner, Phys. Rev. B, Vol.42, pp.9458) Initially, we calculated the argon ion sputtering yield of carbon at 100eV, 300eV and 500eV. For this low energy region, TRIM simulator significantly underestimated the sputtering yields while the yields calculated by the MD simulation agreed well with experimental results. Next, we simulated CF, CF@sub 2@, and CF@sub 3@ ion impacts at 100eV and normal incidence onto an amorphous carbon surface. In all cases, the initial process was net fluorocarbon film deposition at low fluences. For CF@sub 2@ and CF@sub 3@ ions, the fluorocarbon film reached a steady state thickness after several hundred ion impacts. In this talk, we will present the simulated film composition profile and the species that chemically and physically sputter from the surface as a function of ion fluence for each of the three ions simulated. In addition, the angular dependence of both film composition profile and sputtering characteristics will be presented.

9:20am **MS+PS-FrM4 Plasma-Induced Roughening of Resist**, ***S. Halle,*** *W.H. Yan, W. Moreau,* IBM Microelectronics*; J. Wittmann, A. Gutmann,* Infineon Technologies

A severe etch-induced line edge roughness of the resist pattern transfer during dielectric mask open reactive ion plasma processes is increasingly becoming a major issue in semiconductor processing as resist stacks shrink below 700 nm with sub 200 nm lithography. The resulting patterned features are observed to have serrated or "scallop-like" sidewall surfaces which are typically translated from the remaining resist / ARC layer to the dielectric layers and into the silicon, in both device contact-type and active area line space features. The origin of this effect, which results in a roughening of the silicon sidewalls and may severely compromise the patterned feature integrity, is poorly understood. In this study, we show that etch process conditions which produce "scallop-like" distortions are associated with a high degree of resist surface roughness as observed by SEM and measured by AFM. The roughening of a blanket resist surface exposed to reactive ion plasma etching is associated with a large "grain" size in the xy plane and a high "pitting" frequency in the z (depth) axis. The pitting frequency on blanket wafers is found to be qualitatively equivalent to the line edge roughness on patterned features. The extent of roughness is found to be highly sensitive to changes in etch process conditions such as bias voltage, chamber pressure, and gas flow constituents. The resist surface roughness, is examined under the following process conditions: argon sputtering only, fluorocarbon etching with low polymerization, fluorocarbon etching with a higher degree of polymerization. The contribution of the sputter component is found to be dominant; however, polymerizing fluorocarbon chemistry can also modulate the roughness. A qualitative model to explain the formation of the "scallop-like" features will be discussed.

9:40am **MS+PS-FrM5 Measurement of Residual Fluorine in a Polysilicon Etch Reactor with Fourier Transform Infrared Spectroscopy (FTIR)***, **J.E. Daugherty**, E. Edelberg, V. Vahedi, A. Perry, J. Huang, R. Marsh,* Lam Research Corporation

One challenge in sub-0.18 µm gate etching is maintaining the integrity of the thin (<25 Å) gate oxide. This task is especially difficult for in situ hardmask applications where a dielectric (SiO@sub 2@ or Si@sub 3@N@sub 4@) hardmask is etched with a fluorine-containing gas (e.g., CF@sub 4@) in the same chamber that the underlying polysilicon gate is etched with Cl@sub 2@ and HBr. Fluorinated molecules can be released from in-chamber etch residues for several minutes after the fluorine-containing etchant is turned off, and free fluorine is produced when the plasma subsequently dissociates these compounds. If there is sufficient fluorine remaining in the chamber after the polysilicon is etched, it can reduce the selectivity to the underlying gate oxide. A similar reduction of the gate oxide selectivity is often noticed immediately following a dry clean of the etching chamber (i.e., a plasma clean). Since the chamber is cleaned with SF@sub 6@ or NF@sub 3@ plasma, residual fluorine from the cleaning plasma sometimes reduces the amount of remaining gate oxide on the first wafer processed after the clean. We have used Fourier transform infrared spectroscopy (FTIR) to measure the concentration of several fluorine-containing etch products (e.g., SiF@sub 4@, HF) during gate etching with Cl@sub 2@/HBr in an inductively coupled plasma reactor. We have verified that the etch rate of thermal SiO@sub 2@ in Cl@sub 2@/HBr mixtures increases with increasing concentration of residual fluorinated etch products in the effluent of the reactor. We also observe that for in situ hardmask etching, the amount of fluorine-containing etch product that is observed at the end of the polysilicon etch step depends on the duration of fluorine exposure during the hardmask etch step.

10:00am **MS+PS-FrM6 Effect of W Reaction Byproducts on W/poly-Si Stack Gate Etching Process***, **H. Morioka**, M. Nakaishi, N. Abe,* Fujitsu Limited, Japan

W/(barrier layer)/poly Si stack is one of the most promising candidate for gate electrode structure of memory-embedded logic LSIs and DRAMs in the next generation because of low sheet resistance and compatibility with self-aligned contact (SAC) process, etc. Generally, the chemistry of W/poly Si stack gate etching is halogen-base, and most of W etching chemistry have higher etch rate of poly-Si than that of W itself. Although oxygen addition can increase the selectivity to poly Si above 1 by inhibiting Si etching, some troubles are still observed during poly Si etching step, such as non-uniform enhancement of etch rate, undercut profile, and serious RIE-lag. These facts make it difficult to achieve W/poly Si stack gate etching against very thin gate oxide. So, we examined the effect of W reaction byproducts on etching characteristics of other layers. Our experiments were performed on a high-density plasma (HDP) etcher whose plasma source could be operated in continuous mode or pulse modulated mode. We also compared fluorine-base chemistry with chlorine-base one to investigate the difference of etching byproducts. In this experiment, we found that W etching byproducts from a sample wafer and chamber wall enhanced the etch rate of poly-Si and SiO@sub 2@ especially for chlorine-base chemistry, and pulse modulation of plasma could reduce this enhancement. These facts suggest that W etching byproducts were decomposed into fragments in the plasma, these species were deposited on the sample surface and varied the etching characteristics. It is probable that pulse modulation reduced the dissociation of W reaction byproducts because of low electron temperature during afterglow.

10:20am **MS+PS-FrM7 Vacuum- and Near-Ultraviolet Spectra of Plasma Etching Discharges***, **J.R. Woodworth**, T.W. Hamilton, B.P. Aragon,* Sandia National Laboratories

We are measuring the absolute intensities of the Vacuum- and Near- UV emission spectra (24 eV to 4 eV) in metal etch and oxide etch plasmas in an inductively-driven Gaseous Electronics Conference reference cell. These spectra are of interest both because UV radiation may damage the circuits being processed and changes in the spectra may be used for process control. Spectra are being taken both in a cell with stainless steel electrodes and in a cell whose electrodes are covered with aluminum oxide, quartz and silicon to better simulate a commercial etch tool. In metal etch discharges containing mixtures of Cl2, BCl3, Ar, and N2, the vacuum ultraviolet spectrum above 8.8 eV is dominated by atomic Cl lines and Ar lines between 9 and 12 eV. Very little energy is emitted between 12 and 24 eV. The near ultraviolet spectra from 8.8 to 4 eV are dominated by B, BCl, Cl2, and etch products such as Si. Details of the experiments, effects of biasing the wafer, absolute line intensities and the effect of radiation trapping on the discharges will be discussed. This work was supported by the United States Department of Energy under Contract DE-AC04-94-AL85000. Sandia is a multiprogram laboratory operated by the Sandia Corporation, a Lockheed Martin Company, for the United States Government

10:40am **MS+PS-FrM8 Etching of Organic Low Dielectric Constant Materials on the Lam Research 4520XLE***, C. Janowiak, **S.L. Ellingboe**, J. Flanner, I. Morey,* Lam Research Corporation

The low dielectric constant (k) of the polymeric materials SiLK and BCB have made them an attractive possible alternative to silicon dioxide as an intermetal dielectric in IC circuits. The lower dielectric constant is desirable to reduce capacitance and RC delay for higher chip speed, less cross talk, and lower power consumption. The forming of via and trench patterns in these low-k materials using a dry etch chemistry was investigated. Because SiLK and BCB is a polymeric material, oxygen is used as the primary etch gas, nitrogen as a dilulent and a hydrocarbon for sidewall passivation. Typically the organic low-k etch has a selectivity of low-k:PR ~1:1. Depending on the film structure, the PR can clear during the low-k etch, exposing the oxide hardmask for the latter portion of the etch. In the 4520XLE, this corresponds to a change in the etch process from a chemically dominated etch to an ion-dominated etch. Consequently, the plasma chemistry changes upon PR clearing and TEOS exposure, which can result in changes to etch rate, etch rate uniformity, and etch rate profile. Simulations of the SiLK etch results will be shown along with process results. The effects of process parameters such as RF power and oxygen-hydrocarbon ratio on etch performance will be discussed.

Topical Conference on Emerging Opportunities and Issues in Nanotubes and Nanoelectronics

Room 6C - Session NT+NS+EM+MS-FrM

Nanotubes: Growth, Characterization and Properties II

Moderator: R.L. Jaffe, NASA Ames Research Center

8:20am **NT+NS+EM+MS-FrM1 Gas-phase Nanotube Production at High Pressure By Disproportionation of Carbon Monoxide***, **P. Nikolaev**,* G. B. Tech Inc. / NASA - JSC*; M. Bronikowski, K. Bradley, D. Colbert, K. Smith, R.E. Smalley,* Rice University

Single-wall carbon nanotubes (SWNTs) were produced in gas phase, in a flow tube reactor in 3 - 15 atm. of CO at 850@super o@ - 1200@super o@C. Nanotube growth was catalyzed by unsupported iron particles created in-situ by decomposition of iron pentacarbonyl vapor which was added to the CO feedstock at a few ppm level. We find that low Fe(CO)@sub 5@ concentration combined with fast heating rate of feedstock gas allows us to produce very small iron particles, while high pressure increases the rate of CO disproportionation, leading to effective nucleation and growth of SWNTs. Unlike pyrolysis of hydrocarbons, CO disproportionation is a "clean" process which proceeds only on the catalyst surface, resulting in essentially no amorphous carbon overcoating. Diameter distribution of the SWNTs is rather narrow and depends on CO pressure. Higher CO pressures (10 atm.) yield smaller nanotubes, with distribution centered at 0.7 nm (which is roughly the size of C@sub 60@ molecule). Nanotube yield relative to the amount of iron catalyst increases as the heating rate and mixing of Fe(CO)@sub 5@ are enhanced, indicating better catalyst utilization. In order to further increase nanotube yield, we have designed a "shower head" injector, in which cold CO/Fe(CO)@sub 5@

feedstock enters furnace through water-cooled injector, surrounded by "shower head" carrying CO pre-heated to 1200@super o@. Nanotube yield is also increased by addition of small amount of methane, while more CH@sub 4@ results in amorphous overcoating on the nanotube surface. In contrast to previously reported SWNT production methods, this scheme constitutes a continuous flow gas phase SWNT production process. It should therefore be readily amenable to scale up for bulk SWNT production.

8:40am **NT+NS+EM+MS-FrM2 The Optical Properties of Carbon Nanotubes and Their Use in the Characterisation of Bulk SWNT Material*, M.S. Golden*,** *T. Pichler, R. Friedlein, M. Knupfer, J. Fink,* IFW Dresden, Germany*; O. Jost, A.A. Gorbunov, W. Pompe,* TU Dresden, Germany

The investigation of the optical properties of carbon nanotubes,@footnote 1,2@ either using UV-Vis or electron energy loss spectroscopies, offers insight into carbon nanotubes on two levels. Firstly, analysis of the energy positions of the characteristic electronic transitions between the singularities in the density of states enables a quick and easy determination of the overall NT yield, the diameter distribution and the ratio of semiconducting-to-metallic SWNTs in bulk samples. This represents an ideal express characterisation method to accompany tuning of the nanotube preparation process parameters. Secondly, the momentum dependence of the collective excitations of the @pi@-electron system in nanotubes measured using high resolution electron energy loss spectroscopy in transmission proves to be a sensitive probe of the effective dimensionality of the electron system and inter-tube interaction, both in bulk samples of SWNT and MWNT. @FootnoteText@ @footnote 1@ T. Pichler, M. Knupfer, M. S. Golden, J. Fink, A. Rinzler, R. E. Smalley, PRL 80 4729 (1998) @footnote 2@ T. Pichler, M. Sing, M. Knupfer, M. S. Golden, J. Fink, Solid State Commun., 109, 721 (1999).

9:00am **NT+NS+EM+MS-FrM3 Li Intercalated Carbon Nanotubes Ropes***, J. Lu, J. Zhao,* ***A. Buldum****, B. Gao, O. Zhou,* University of North Carolina, Chapel Hill **INVITED**

The electronic and electrochemical properties of Li intercalated single-wall nanotube ropes are studied theoretically using ab initio method@footnote 1@ and experimentally in an electrochemical cell.@footnote 2@ Complete charge transfer is found between Li atoms and nanotubes. The energetic and electrochemical potential of intercalated Li atoms on both the inside and the outside of tubes are investigated. The intercalated ropes are metallic with conduction band resides on C atoms. Both theoretical and experimental studies suggest that it is possible to achieve a Li intercalation density significant larger than that in the graphite, making the Li intercalated nanoropes a promising material for battery applications. @FootnoteText@ @footnote 1@ J. Zhao, A. Buldum, J. P. Lu, to be published. @footnote 2@ B. Gao and O. Zhou, to be published.

9:40am **NT+NS+EM+MS-FrM5 Mechanical and Electronic Properties of Carbon Nanotubes Under Bending*, L. Yang*,** *M.P. Anantram, J. Han, R.L. Jaffe,* NASA

Bending, buckling and even collapsing of carbon nanotubes have been more frequently observed experimentally. They could be elastic or plastic deformations, and responsible for a variety of mechanical and electronic measurements. We systematically investigate mechanical and elecronical properties of carbon nanotubes under these deformations. They are correlated with tube configuration and stress - strain relations. Some interesting observations are made. For example, electron transport can be enhanced or suppressed, depending on the configuration and deformation of a tube. We also apply the simulation results in understanding some related experimental observations.

10:00am **NT+NS+EM+MS-FrM6 Effect of Strain on Electrical Properties of Carbon Nanotubes*, S. Paulson*,** *N. Snider, M.R. Falvo, A. Seeger, A. Helser, R.M. Taylor III, R. Superfine, S. Washburn,* University of North Carolina, Chapel Hill

We have used an advanced interface to an Atomic Force Microscope to apply strain to carbon nanotubes. Simultaneously, we measure the current voltage characteristics, and see how they change as a function of strain in the tube. We have applied enough strain to fracture nanotubes, causing the resistance to become infinitely large, and then reassembled the ends to form junctions. The characteristics of these junctions will be discussed, as well as other strain dependant effects.

10:20am **NT+NS+EM+MS-FrM7 Molecular Dynamics Simulation of the Thermal Conductivity of Carbon Nanotubes*, M.A. Osman,*** NASA Ames Research Center, US*; D. Srivastava,* NASA Ames Research Center

Carbon nanotubes (CNT) have very attractive electronic, mechanical, and thermal properties. Recently, measurements of thermal conductivity in single wall CNTs showed thermal conductivity magnitudes ranging from 17.5 to 58 W/cm-K at room temperature, which are better than bulk graphite.@footnote 1@ The cylinderical symmetry of CNT leads to large thermal conductivity along the tube axis which is an improvement over the strongly anisotropic nature of thermal conductivity of graphite. Additionally, unlike graphite, CNTs can be made into ropes that can be used as heat pipes. We have investigated the thermal concutivity of single wall CNTs Using non-equilibrium molecular dynamics (MD) with Brennar potential. The results of the simulation are in good agreement with the experimental results. We will discuss the results of our simluation and report on the effects of tube diameter and chirality on the thermal conductivity. @FootnoteText@ @footnote 1@ J. Hone, M. Whitney, C. Piskoti, and A. Zettl, Phys. Rev. B59, R2514 (1999).

10:40am **NT+NS+EM+MS-FrM8 Materials Applications of Carbon Nanotubes: Hydrogen Storage and Polymer Composites*, S.J.V. Frankland,*** *D.W. Brenner,* North Carolina State University

Simulations addressing two applications of carbon nanotubes will be presented. Nanotubes have been proposed as storage media for hydrogen in fuel cells. Experiments have shown that the nanotube samples contain more hydrogen than will fit densely packed into the tubules themselves. Therefore, the location of the hydrogen is in question. The Raman shift of the hydrogen may provide a useful indicator of its placement. So far, two qualitative trends have been identified with molecular dynamics simulation which should enable the distinction of internal versus intercalated hydrogen. For internal hydrogen a decreasing Raman shift is observed with increasing nanotube radius. For intercalated hydrogen, the simulations predict a broadened Raman band with relatively little dependence on nanotube radius. The second application being considered is the usage of nanotubes to strengthen polymer composites. Molecular dynamics simulations are in progress to understand the load transfer mechanism between the polymer and the nanotube.

Plasma Science and Technology Division
Room 609 - Session PS-FrM

Emerging Plasma Applications

Moderator: W.M. Holber, Applied Science and Technology, Inc.

8:20am **PS-FrM1 Plasma Doping for Shallow Junctions*, S.B. Felch*,** *M.J. Goeckner, Z. Fang,* Varian Semiconductor Equipment Associates*; G.C.-F. Yeap, D. Bang, M.-R. Lin,* AMD Inc. **INVITED**

This paper reviews the characteristics of ultra-shallow junctions produced by Plasma Doping (PLAD). PLAD is one of the alternate doping techniques being developed for sub-0.18 µm devices. In the PLAD process, the substrate is placed directly in a plasma that contains the desired dopant ions. A negative-bias pulse is used to drive the dopant ions from the plasma into the substrate. Here, we describe results from a wide range of experiments aimed at the production of ultra-shallow junctions for sub-0.18 µm devices. For the results shown here, a BF@sub 3@ plasma was used to provide the dopant ions that were driven into 200-mm Si substrates using wafer biases ranging from -0.14 to -5.0 kV. The ultra-shallow junctions formed with this technique hav e been examined with both SIMS and electrical profiling techniques. Good sheet resistance uniformity, charging performance, and added contamination levels have been obtained. When PLAD is used in the production of sub-0.2 µm gate length pMOSFETs, one finds sub-threshold swing, off-state leakage, and hot-carrier reliability similar to beamline-implanted ones. In addition, higher drive currents are seen in the plasma-doped devices. These results together with the expected small footprint and low cost-of-ownership of such a system make PLAD an attractive doping technique.

9:00am **PS-FrM3 Sputter-Wind Heating in Ionized Metal PVD@footnote 1@*, J. Lu,*** *M.J. Kushner,* University of Illinois, Urbana

Ionized metal physical vapor deposition (IMPVD) is used to deposit seed layers and/or diffusion barriers in high aspect ratio trenches and vias for microelectronics fabrication. The physical sputtering is generated from a magnetron cathode. A secondary plasma is generated between the cathode and the substrate by an rf antenna. Experimental measurements suggest that sputter heating, generated by momentum and energy transfer from the sputtered metal atoms and the background gas atoms, rarifies the background gas and affects the transport of the sputtered atoms. In this study, sputter wind heating in IMPVD reactors is investigated using the Hybrid Plasma Equipment Model (HPEM) which has been improved to include processes relevant to sputter heating. These processes include ion energy-dependent yield, ion-energy dependent sputtered atom kinetic energy distribution, and heating due to the sputtered atoms. Improved algorithms have also been developed for electron transport in high magnetic fields to fully resolve the magnetron effect. The transport of the sputtered atoms is treated with a Monte-Carlo simulation. Statistics are collected on the interaction of sputtered atoms with the background gas, and are used to generate source terms in the continuity, momentum, and energy equations. Parametric studies have been performed for sputter heating in aluminum and copper IMPVD systems operating at low to high powers (up to 1500 W ICP, and 2000 W magnetron), and low to high reactor aspect ratio (height to radius) in 10's mTorr Ar. Due to the rarefaction in front of the target which results from sputter-wind heating, the slowing down length for sputtered atoms increases, thereby changing the flux of sputtered atoms to the substrate. Commensurate changes in the ion current to the target shift its I-V characteristics. @FootnoteText@ @footnote 1@This work was supported by SRC and TAZ.

9:20am **PS-FrM4 Opportunities and Challenges for Plasma Processes in MEMS Fabrication*, J.J. Sniegowski,*** Sandia National Laboratories **INVITED**

MicroElectroMechanical Systems (MEMS) are a burgeoning area of device development that has growing commercial applications in automotive, medical, and display technologies, with the promise of vigorous near-term expansion into areas such as information systems, chemical analysis, and consumer products. Microsystems present an arena for the emergence of new plasma processing techniques, especially in the demanding area of etching. Today's most prevalent IC-based fabrication method is multilayer polysilicon surface micromachining. Plasma etch processes for defining structures in surface micromachined films comprise critical fabrication steps and must evolve to enable advances in microsystem capability. Typical plasma etch processes in surface micromachining will be outlined in terms of requirements like etch profile, aspect ratio, selectivity, and etch rate for several illustrative MEMS devices. Future etch demands such as submicron spaces with aspect ratios greater than 10, polysilicon films more than 6 microns thick, and large mask open areas will be described. In fact, the needs for vertical sidewalls and simultaneous clearing of both small (1 micron) and large (>10 microns) spaces, without any micromasking, already challenge conventional plasma tools and processes. Lastly, extremely deep silicon etching for very high aspect ratio structures, or through-wafer vias for material or optical transmission, interconnect, or environmental exposure will be discussed as perhaps the most difficult task for plasma etching technology. Although the time-multiplexed "Bosch" process has been viewed as a major breakthrough for the deep silicon etch application, opportunities remain for refinements, or alternatives employing more conventional etch tools.@footnote 1@ @FootnoteText@ @footnote 1@Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract No. DE-AC04-94AL85000.

10:00am **PS-FrM6 200 mm SCALPEL@super TM@ Mask Dry Etch Development*, G.R. Bogart,*** *A. Kornblit,* Lucent Technologies*; I. Johnston,* Surface Technology Systems, UK*; A.E. Novembre, M.L. Peabody, C.S. Knurek, R.J. Kasica,* Lucent Technologies

SCALPEL (SCattering using Angular Limitation Projection E-beam Lithography) is based on the variation in scattering angles between two electron transparent materials supported on a membrane mask.@footnote 1@ Plasma etching of the membrane structure offers many advantages over wet etching using KOH. We have used a Time Multiplexed Deep Etching (TMDE) technique (Bosch process)@footnote 2,3@ for generation of large area thin (200:1 with a side wall angle of 89°. Etch uniformity is

10:20am **PS-FrM7 High Anisotropy Etching of 0.18 Micron Platinum Electrodes*, S.D. Athavale,*** *D.E. Kotecki,* IBM, Microelectronics Division*; H. Shen,* Siemens*; J. Hwang, C. Ying, D.J. Lee, S. Mak,* Applied Materials, Inc.

Platinum is one of the most promising electrode materials for future high density DRAM capacitors based on high dielectric constant materials such as BST. Achieving veil-free, vertical sidewall profiles, when dry etching platinum, has remained an elusive goal due to the low volatility of etch-products under traditional plasma etching conditions. We have studied etching of platinum using a high-density plasma reactor equipped with a high temperature (>200°C) cathode. Statistical design of experiments (DOE) methodology was used. It has been found that the result of etching Pt is strongly influenced by the wafer temperature. For example, increasing the wafer temperature leads to a dramatic increase in the Pt etch rate and a change in resulting Pt profile. Nearly vertical sidewall profiles (89°) and veil-free Pt etching results are achieved on 0.18µm electrode. The key wafer-level issues and integration challenges associated with the etching of Pt electrodes under high temperature conditions are also discussed.

10:40am **PS-FrM8 Real Time Control of Plasma Tools During Recipe Changes and Transients@footnote 1@*, M.J. Kushner,*** University of Illinois, Urbana*; S. Rauf,* Motorola Inc.

Successful development of real time control (RTC) of plasma tools should enable more rapid process development. A full etch process often includes multiple recipe changes to optimize, for example, break-through, main etch and over-etch. If the recipes are markedly different in gas composition or pressure, process parameters such as uniformity may significantly change during the transient. In the absence of RTC, maintaining desired process parameters requires changes in actuators based on interpolation between the beginning and end conditions. In this paper, the Virtual Plasma Equipment Model (VPEM) is used to investigate RTC strategies during recipe changes and transients. The VPEM is a "wrapper" for the Hybrid Plasma Equipment Model which contains simulated sensors, controllers and actuators. Recent improvements in the VPEM allow investigation of "real-time" (as opposed to run-to-run) control. Results from the VPEM will be discussed using response-surface based controllers to maintain process uniformity and rate during recipe changes for Cl@sub 2@ and C@sub 2@F@sub 6@ chemistries in ICP reactors. It was found that during recipe changes which, for example, significantly change mole fractions, the linearized response surfaces based on conditions at any given mole fraction are not adequate. Control is maintained for a portion of the transient but is eventually lost. To address this problem, real time mass spectrometer sensor data is used to interpolate between response surfaces which are the basis of (2 x 2) controllers. The response surfaces were generated using results from steady-state experiments. This strategy was able extend the dynamic range of control throughout the transient. @FootnoteText@ @footnote 1@This work was supported by AFOSR/DARPA, SRC and LAM Research.

11:00am **PS-FrM9 Plasma Injection with Small Helicon Sources*, F.F. Chen,*** University of California, Los Angeles*; X. Jiang,* Broadcom, Inc.

Distributed plasma sources for large-area etching and deposition, comprising multiple helicon injectors, have been shown to be feasible.@footnote 1@ In this experiment, we studied the coverage provided by a single small source, varying the magnetic field and antenna configurations. The source was a 2.2 cm i.d., 12 cm long pyrex tube tightly covered by a thin, 3.9 cm i.d. solenoidal magnet coil providing up to a B = 100G field. A helical antenna was normally used to launch right-hand circularly polarized waves with 0-1000 W of 13.56 or 27.12 MHz power. The argon plasma was injected into to a 30 cm diam chamber with or without a permanent magnet "bucket". The low-field density peak@footnote 2@ usually found in helicon sources was not seen; instead, the maximum density almost always occurred at B = 0, as in ordinary ICPs. However, the densities were in the 10@super 11-12@ cm@super -3@ range characteristic of helicon sources. These were indeed helicon discharges, and the absence of a low-field peak was explained by detailed mapping of the magnetic field. With close-fitted solenoids, the plasma created near the edge of the source was scraped off by the entrance flange or was brought back to the top plate once the magnetic field became strong enough to entrain the electrons. At the higher fields, only the plasma created near the axis was available to a downstream probe. The high efficiency of helicon sources can be made available by properly designing the magnetic field coils so that all the field lines reach the interior of the downstream region and then diverge before striking the substrate. @FootnoteText@ @footnote 1@F.F. Chen and J.D. Evans, Proc. Plasma Etch Users Group (NCCAVS, 150 W. Iowa Ave., Suite 104, Sunnyvale, CA 94086) (1998). @footnote 2@F.F. Chen, J. Vac. Sci. Technol. A 10, 1389 (1992). .

11:20am **PS-FrM10 Ultra-Low-Temperature Formation of Silicon Nitride Gate Dielectric Films by Novel Plasma Technique*, M. Hori,*** *H. Ohta, A. Nagashima,* Nagoya University, Japan*; M. Ito,* Wakayama University, Japan*; T. Goto,* Nagoya University, Japan

As device dimensions shrink below 100nm in ULSI, the thickness of gate dielectric film (SiO@sub2@) in FETs will fall to be 2-3nm range. The SiO@sub2@ film is replaced by a dielectric film with a higher dielectric constant film. In this study, we have successfully formed the ultra thin silicon nitride (SiN@subx@) films of 5nm in thickness at a low temperature of 300 degree C by the novel plasma technique using ECR

SiH@sub4@/N@sub2@ plasma enhanced CVD (PECVD), where the charged species incident on the substrate were removed by two permanent magnets set above the substrate. It enabled us to form SiN@subx@ films by only neutral radicals. The experimental conditions were 0.5Pa, 300W, SiH@sub4@/N@sub2@ of 5/100sccm, and a substrate bias of floating. The films indicated the low leakage current of 7x10@super-8@A/cm@super2@ at 3MV/cm, dielectric constant of 7.3 and near stoichiometry composition. The reaction mechanism of film deposition with and without charged species were investigated by in-situ XPS and in-situ FT-IR reflection absorption spectroscopy. In the case of without charged species, two absorption bands ascribed to Si-N stretching mode at 970cm@super-1@ and 1085 cm@super-1@ were observed. The low frequency component is probably due to the metastable layer and the high one is due to the SiN@subx@ network. On the other hand,with charge species, the only low component was observed. The metastable layer is considered to cause the degradation of electrical properties of films. On the basis of these results, the control of ion bombardment on the growth was found to be a key factor for forming ultra thin SiN@subx@ films of high quality at a low temperature in PECVD.

11:40am **PS-FrM11 Characterizations of a Compact, Low-Field Toroidal Plasma Source for Downstream Plasma Processing***, **X. Chen**, W.M. Holber, D.K. Smith,* Applied Science and Technology, Inc.*; M.G. Blain, R.L. Jarecki,* Sandia National Laboratories

Activated atomic gases are used in semiconductor processing for applications including photoresist strip, passivation and chemical vapor deposition (CVD) chamber clean. We report the production of activated atomic fluorine, oxygen, nitrogen and hydrogen using a low-field toroidal (LFT@super TM@) downstream plasma source. The ASTRON@super TM@ reactive gas generator uses an electrodeless toroidal plasma source design, in which the rf power supply is integrated directly into the same enclosure as the plasma source. It operates at pressures from a few millitorr to one atmosphere. Typical plasma density is 3x10@super 13@ cm@super -3@. Thorough characterization of the plasma source is conducted using working gases such as NF@sub 3@, CF@sub 4@, CHF@sub 3@, C@sub 3@F@sub 8@, SF@sub 6@, O@sub 2@, N@sub 2@, NH@sub 3@ and H@sub 2@. The production and transport of the atomic species are investigated using chemiluminescent titration and etch rate measurements of silicon dioxide and photoresist. Greater than 90% of NF@sub 3@ is dissociated at flow rates of over 2 slm. The etch rates of SiO@sub 2@, SiN, WN, W and TiN are measured. Adding argon to an O@sub 2@/N@sub 2@ plasma increases the production of atomic oxygen and the rate of photoresist strip while not raising the power consumption. Contamination and particle measurements show that the plasma source is compatible with semiconductor processing. @FootnoteText@ Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract No. DE-AC04-94AL85000.

Surface Science Division
Room 606 - Session SS1+AS+BI-FrM
Organic Films/Self-Assembled Monolayers

Moderator: G.E. Poirier, National Institute of Standards and Technology

8:20am **SS1+AS+BI-FrM1 Simple Viscosity Model Analysis of Hydronium Ion Motion in Nanometer Organic Films***, **K. Wu**, M.J. Iedema, J.P. Cowin,* Pacific Northwest National Laboratory

Nanometer organic films such as methylcyclohexane and 3-methylpentane were vapor-deposited at 30 K on Pt(111) with a molecular beam. Pure hydronium ions were soft-landed on top of the films at a kinetic energy less than 1.2 eV. The voltage change and desorption of the organic films were simultaneously monitored by a Kelvin probe and a mass spectrometer. Ion dosing on the organic films was a capacitive charging process, therefore the film voltage change actually reflected the ion motion in the organic films, assuming the dielectric constants of the organic films do not change much with temperature. When the films were warmed, ions gradually moved into the films. The experimental results were analyzed by a simple viscosity model. To a large extent, the temperature (or time) evolution of the film voltage could be well predicted by the model. The film voltage fall-off temperature width from the theory was, however, about half of that from the experiment. Further experimental evidence showed that the ion self-generated electric field strength had a strong effect on the ion motion. For example, when the electric field strength was higher than 0.05 V/Angstrom, the theoretical prediction seriously deviated from the experimental result, indicating that a high electric field might trigger non-linear ion motion and made the Stokes-Einstein equation not accurate. When films were prepared at higher temperatures, methylcyclohexane could crystallize on Pt(111), making ions more difficult to transport in the crystalline films. But, 3-methylpentane never crystallized before ion motion in it completed, indicating that it's a good glass material. With this general approach, we could attack many important issues such as ion motion across liquid-liquid interfaces, hydration of ions and so on.

8:40am **SS1+AS+BI-FrM2 Direct Observation of Topological Defect Evolution and Domain Motion in Ultrathin Films of PS-b-PMMA Diblock Copolymers Using Atomic Force Microscopy***, **J. Hahm**[1], W.A. Lopes, H.M. Jaeger, S.J. Sibener,* The University of Chicago

We report the tracking of individual topological defects in the microdomain patterns of cylinder-forming polystyrene-block-polymethylmethacrylate (PS-b-PMMA) films. These films undergo vertical and lateral phase separation when they are thermally annealed. The vertical phase separation results in thickness quantization where each layer exhibits its own topology and dynamics. The lateral phase separation provides height contrast between the two components of the diblock in single-cylinder-layer thick films. In the atomic force microscopy (AFM) topographic images, the PMMA is higher by approximately 1nm as compared to the PS blocks. 50nm thick films, containing a single layer of cylinders aligned parallel to the film plane, were repeatedly and non-destructively probed with AFM in an attempt to elucidate the evolution of the diblock domain topology between annealing treatments. We show explicitly that the evolution of topological defects takes place through relinking, joining, clustering and annihilation of defects. Such processes form the basis for predicting structural changes in polymer thin films. We also have used time-lapse AFM imaging to observe directly the kinetics of domain mobility responsible for topological evolution. Domains of different thicknesses were monitored as a function of annealing temperature and time. The higher mobility and lower activation energy associated with thicker domain mobility are accounted for by the essentially negligible substrate interactions where polymer-polymer rather than polymer-substrate interactions govern the dynamics. Our hope is that the combined understanding of topological changes, such as those reported in this talk,when combined with mobility kinetics, will give us a predictive understanding of the thermally activated structural changes that occur within thin polymer films. @FootnoteText@ Supported by the NSF-MRSEC at the University of Chicago and AFOSR.

9:00am **SS1+AS+BI-FrM3 Properties of Self-Assembled Monolayers of Biphenyl-Based Thiols***, **T. Felgenhauer**, H.-T. Rong, M. Buck, M. Grunze,* University of Heidelberg, Germany

Despite their versatility to modify surface properties, self-assembled monolayers (SAM) based on alkane thiols have limitations concerning conformational stability or structural perfection. In search for more rigid molecules, thiols based on aromatic moieties offer an alternative. However, in contrast to SAMs consisting of alkane thiols experiments on aromatic thiols are relatively scarce. Our experiments focus on thiol SAMs consisting of 4,4'-substituted biphenyls (BP). To allow systematic investigations the number of methylene units between the biphenyl moiety and the thiol group was varied between zero and six. The electrochemical behavior of BP-SAMs turns out to be very different from alkane thiols. In general, the charge permeability of BP-SAMs is higher by orders of magnitude even though the electrochemical stability of BP-SAMs is dependent on the methylene spacer. Exposure to an etching solution reveals a stability significantly higher compared to alkane thiols and suggests an improved structural perfection of BP-SAMs. Spectroscopic characterization of the BP-SAMs yields an orientation of the biphenyl units alternating with the methylene chain length. Comparison of BP-SAMs on Au with those on Ag shows a reversal of the odd-even effect and demonstrates that the sulphur-substrate bond is crucial for the molecular orientation of the biphenyl-SAMs.

9:20am **SS1+AS+BI-FrM4 Structure of Self-assembled Monolayers of Alkanethiols and Disulfides on Au(111)***, **H. Nozoye**,* National Institute of Materials and Chemical Research, Japan*; C. Kodama, T. Hayashi,* University of Tsukuba, Japan

Self-assembled monolayer (SAM) films of alkanethiols and alkyldisulfides have been attracting an increasing interest. However, we do not have a concrete picture of SAM, e.g. is the SH bond broken on the surface ? , is the SS bond formed on the surface ?, or where is the adsorption site of S ?. We studied these problems by means of STM, HREELS, high-sensitivity LEED,

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

and TPD. Alkanethiols (C1-C10) and alkyldisulfides (C2-C12) were adsorbed on a Au(111) single crystal surface at room temperature or at around 120 K. Dersorption of H2, parent alkanethiol, alkylthiolate radical, and alkyldisulfide were observed in TPD and a vibration peak assigned to a SS bond was missing in HREEL spectra. We clearly concluded that the SH bond of alkylthiols breaks at low temperature forming alkylthiolates on the surface. Furthermore, the SS bond of alkyldisulfides was shown to be broken on the surface, forming alkylthiolate. The Au-S bond of alkylthiolates on the surface gave a relatively strong peak in HREEL spectra. We will discuss the formation process and the relation between the local structure and the long-range order of SAM.

9:40am **SS1+AS+BI-FrM5 Toward Vapor Deposition of Polycyanurates: The Surface Chemistry of Phenyl Cyanate and Phenol on Al(111)***, B. Bartlett, J.M. Valdisera,* ***J.N. Russell, Jr.,*** Naval Research Laboratory

Polycyanurates, formed by polymerization of monomers containing two cyanate groups, show promise as vapor depositable, low dielectric parameter materials for microelectronics applications. Consequently, we are examining the chemistry of a model system, phenyl cyanate on Al(111) surface, with temperature programmed desorption (TPD), Auger electron spectroscopy (AES), and X-ray photoelectron spectroscopy (XPS). (Aluminum was chosen as a substrate because it is used for interconnects in microelectronics.) For submonolayer coverages, XPS shows that the phenyl cyanate undergoes O-CN bond cleavage between 150 and 200 K, leaving phenoxide and cyanide groups on the surface. Benzene and hydrogen decomposition desorption products were observed at 620 K, and between 500 and 800 K, respectively. This is analogous to the reaction of phenol on Al(111). Deuterium labeling was used to determine the sequence of C-H bond scission on the phenoxy species. XPS and AES reveal the formation of aluminum oxide, nitride and carbide on the surface above ~ 400 K. After multilayer exposures, the formation of the phenyl cyanate trimer, triphenoxytriazine, was observed with XPS between 160 and 200 K. The trimerized multilayer was stable up to ~ 500 K before it decomposed. This data suggests that at high coverages, a dicyanate functionalized molecule may chemically attach to aluminum by cleavage of an O-CN bond, while the other cyanate group is available for trimerization, thus anchoring a polycyanurate film to the surface. The surface chemistry of a dicyanate functionalized molecule, 1,1-bis(diphenylcyanato)ethane, is currently under investigation to confirm this hypothesis.

10:00am **SS1+AS+BI-FrM6 Formation of Organic Layers by Cycloaddition Reactions at Germanium Surfaces***, S.W. Lee,* University of Missouri, Columbia*; J.S. Hovis, R.J. Hamers,* University of Wisconsin, Madison*;* ***C.M. Greenlief,*** University of Missouri, Columbia

The formation of ordered organic layers on Ge(001) substrates is explored. Ge substrates are prepared by a novel method and exposed to a variety of cyclic hydrocarbons, including cyclopentene and cyclohexene. The subsequent surface interactions are followed by a variety of surface sensitive techniques. Bonding configurations are determined by photoelectron spectroscopy and scanning tunneling microscopy. The strength of surface interactions are also monitored by temperature programmed desorption. Cyclopentene and cyclohexene react with Ge dimer bonds via a [2+2] cycloaddition reaction. This reaction generates rows of the surface complex oriented along the dimer bond direction of the Ge(001) surface, which is easily observed by scanning tunneling microscopy. Experiments using other cyclic hydrocarbons and attempts at further surface modification will be discussed.

10:20am **SS1+AS+BI-FrM7 Multilayer Phases in Self-Assembled Monolayers Based on Silane Coupling Agents***,* ***B.C. Bunker,*** *R.W. Carpick, M. Hankins, M.L. Thomas, R. Assink, M. DeBoer,* Sandia National Laboratories

Thin films prepared using silane coupling agents are used extensively to chemically modify surfaces. In micromachines, such films are used to control stiction, friction, and adhesion of moving parts. The films are commonly depicted as self-assembled monolayers, in which each silane molecule forms extensive Si-O-Si linkages to the surface and to other molecules. However, many workers report that it is difficult to produce self-assembled monolayers on a reproducible basis, especially for films having fluorinated hydrocarbon chains. In this paper, atomic force microscopy studies are used to show that irreproducible film formation is associated with the fact that silane coupling agents can self-assemble into a range of structures described in common surfactant phase diagrams. Evidence is presented suggesting that hydrocarbon and fluorocarbon silanes form lamellar and inverse micelle structures on silica and silicon nitride surfaces. In some instances, multilayer structures are produced during fabrication. Films which start out as monolayers can also reorganize into multilayer phases after deposition. Factors influencing the phases observed include surface pretreatment, the solvent, silane and water concentrations in the deposition solution, and environmental parameters such as temperature and relative humidity. Mechanisms for the evolution of the observed range of self-assembled structures vs. reaction conditions are described.

10:40am **SS1+AS+BI-FrM8 Self-assembled Monolayers on Silicon Surfaces: The Opposite to Siloxane Chemistry***,* ***J.A. Mulder,*** *R.P. Hsung, X.-Y. Zhu,* University of Minnesota

Self-assembled monolayers (SAMs) on silicon surfaces are of interest for a number of reasons: they may be used as monolayer resists in high resolution lithography, as dielectric layers, as active components in hybrid sensor devices, as passivation and lubrication layers in MEMS, and as a new platform for biochips. SAMs on silicon are traditionally formed via siloxane chemistry on oxidized surfaces from organosilicon derivatives, such as alkyltrichlorosilane. The problems with siloxane SAMs are well known: they are difficult to prepare and suffer from poor reproducibility; the contradiction between cross-linking and close-packing is inherent; the presence of the amorphous and insulating oxide layer is not desirable in some applications. There is much incentive to develop simple processes for the formation of stable molecular layers directly on the silicon surface. We present a novel approach which, in essence, is the opposite to the siloxane SAM process. The assembly processes are based on the reaction between R-OH or R-NH2 with chlorinated silicon surfaces, leading to molecular assembly via Si-O or Si-N linkages. These reactions are not only efficient but also sufficiently versatile for the assembly of a wide variety of functional organic molecules. A particular advantage of this new assembly chemistry is that it is compatible with both vacuum and solution phases and can be carried out under very benign experimental conditions. We characterize these SAMs using a variety of techniques, such as multiple-internal reflection FTIR, X-ray photoelectron spectroscopy, contact angle measurements, and scanning probe microscopy. We address structural and stability of these SAMs and their dependence on molecular structure, such as alkyls and aromatics. We also discuss immediate and future applications.

11:00am **SS1+AS+BI-FrM9 The Photochemistry of Model Organosulfur Compounds Adsorbed on GaAs (110): Energy-Resolved Photofragment Angular Distributions***,* ***N. Camillone III,*** *K. Adib, R.M. Osgood, Jr.,* Columbia University

Self-assembled monolayers of organothiols and related compounds hold promise for use in the semiconductor industry as ultrathin electron beam resists and precursors for the growth of II-VI materials, as well as for the growth of passivating gallium sulfide films on GaAs. An understanding of the structure and photon and electron chemistry of organothiols and related compounds is relevant to the development of these technologies. We report on our studies of the photoinduced chemistry of three model organosulfur compounds, CH@sub 3@SH, (CH@sub 3@S)@sub 2@ and CH@sub 3@SCH@sub 3@, on the (110) surface of GaAs. We find that the cross sections for the photoinduced reactions of these molecules in the adsorbed monolayers follows the trend CH@sub 3@SH > CH@sub 3@SCH@sub 3@ > (CH@sub 3@S)@sub 2@. Comparison of these measurements to photoinduced chemistry in the multilayer regime gives insight into the degree to which close proximity to the semiconductor surface perturbs the photochemistry. In addition, the structure and molecular orientation of these molecules is discussed in light of the results of energy-resolved photofragment angular distributions and low energy electron diffraction measurements. The post-irradiation chemistry of the trapped photofragments will also be discussed.

Surface Science Division
Room 607 - Session SS2-FrM

Adsorption on Metals and Silicon

Moderator: A.A. Baski, Virginia Commonwealth University

8:20am **SS2-FrM1 Quantitative Determination of Adsorbate Interactions on an Iron Surface***, L. Österlund, M.O. Pedersen, I. Stensgaard, E. Laegsgaard,* ***F. Besenbacher,*** University of Aarhus, Denmark

We introduce a new concept of Configuration Distribution Analysis (CDA) to extract quantitative values of the adsorbate-adsorbate interaction potential from Scanning Tunneling Microscopy (STM) data. By analyzing atomically resolved nitrogen islands on a Fe(100) surface, we show that the propensity of small, compact c(2x2) islands is due to a many-body effect in combination with elastic interactions. It is shown that the nearest and next-nearest neighbour interactions are strongly repulsive and weakly attractive, respectively, where the latter is modulated by the nearest neighbour coordination. Accurate determination of adsorbate-adsorbate interactions are essential to understand a variety of surface phenomena, and until now, there has been a lack of reliable experimental results. The results presented here promise to provide a new tool to bridge this gap.

8:40am **SS2-FrM2 CO Adsorption on Mn Films on Cu(100)***, **M. Grüne**,* Universität Bonn, Germany*; G. Boishin,* Bulgarian Academy of Sciences, Bulgaria*; R.-J. Linden, T. Pelster, J. Breitbach, A. Frey, C. Becker, K. Wandelt,* Universität Bonn, Germany

The adsorption of carbon monoxide on Mn films on Cu(100) at 100 K was studied by means of UPS, HREELS, LEED, TDS, and work function change measurements. On the c(8x2) Mn monolayer, two stages of adsorption can be separated. The first type of molecularly adsorbed CO increases the work function by 0.9 eV. HREEL spectra resolve at least 4 different adsorption states, which cannot be separated by dosing or annealing. We assign these to side-on CO, step sites, and different kinds of bridge-bonded sites. The substrate superstructure remains intact in this low-coverage range. No adsorbate-induced LEED spots can be observed. Further CO adsorption beyond a critical exposure leads to a destruction of the Mn film order accompanied by a change of the CO-metal interaction as revealed by UPS and a decrease of the work function by 0.16 eV. In HREELS an additional CO state can be identified, presumably ontop-CO. At submonolayer Mn coverages, CO adsorbs simultaneously on both Cu and Mn patches. A thick polycrystalline Mn film exhibits molecular adsorption preferably in the side-on geometry. Annealing of CO-covered monolayer films leads to a restructuring of the surface around 220 K, subsequent dissociation of CO around 300 K, accompanied by desorption with a maximum at 350 K. It is not possible to re-establish the ordered film structure by annealing. At submonolayer Mn coverages, an additional desorption maximum at 420 K can be attributed to CO desorption from the Mn island edges. If the surface has not been saturated with CO, molecules change from Cu to Mn sites upon annealing to 160 K. Annealing a CO-covered thick polycrystalline Mn film leads to complete CO dissociation around 210 K.

9:00am **SS2-FrM3 STM Tip Induced 1D Chains on H-covered Ni(100) Surface***, **T. Komeda**, M. Kawai,* The Institute of Physical and Chemical Research (RIKEN), Japan

The adsorption of H on metal surfaces is considered as a weak chemisorption in general, based on its low desorption temperature. Due to its weak bonding, the surface reconstruction on H adsorption is observed only for very open surface, such as (110) surface of fcc transition metal. It has been shown that the H saturated Ni(110) surface at room temperature shows streaky (1x2) superstructure, on which high resolution STM observation showed added and missing rows as the origin of its structure. In this paper, we show STM tip can create very characteristic 1D chains of protrusion and depletion on H-saturated Ni(100) surface; Ni(100) surface is believed to be stable for H adsorption and forms no reconstruction. The 1D structure is apparently similar to the added and missing row structure on H saturated Ni(110) surface. Experimentally clean Ni(100) surface was exposed to 10 L(1L=10-6 torr s) of H2 at 100 K and observed with low temperature STM which is cooled with liquid nitrogen. When the surface is scanned with a very small gap between the tip and the sample (scanning condition such as -1 mV biased on the sample and tunneling current of 4nA), straight protruded rows accompanying depleted rows besides them appear. The height of the protruded row is 0.3-0.5 A, and the high resolution image shows it is composed of a chain of single atoms spaced with 2x1 periodicity. The characteristic 1D structure is similar to the added and missing row structure formed on H saturated Ni(110) surface, and apparently slight touch of the STM tip on the substrate can dig a single row and the released NiH species form added row. As can be seen in the apparent low height of 0.3-0.5 A for the added row on the terrace, the added row and the missing row shows strong bias dependence in the STM image, which indicates very characteristic electronic structures appeared on this quasi 1D structure.

9:20am **SS2-FrM4 Morphology and Electronic Structure of 1D Ca-induced Rows on the Si(111) Surface***, **M.S. Turner**, K.M. Jones, A.A. Baski, J.A. Carlisle,* Virginia Commonwealth University

Deposition of highly reactive alkaline-earth adsorbates (Ca, Sr, Ba) onto semiconductor substrates leads to reconstructions which are row-like in nature. The Ca/Si(111) system has been studied using RHEED, STM and synchrotron radiation photoemission. For Ca coverages less than 0.5 ML, a series of odd-order nx1 (n=3,5,7...)reconstructions have been observed. The most stable of these is a (3x1) phase that occurs at 0.33 ML. Various models have been proposed for the general metal/Si(111)-(3x1) system, and we discuss the accuracy of these models as they apply to this system.@footnote 1@ In particular, we discuss how well the models can be altered to account for the higher-order reconstructions that are observed at higher Ca coverages, and for commonly observed defect structures in the (3x1) phase. These objectives are accomplished through comparison between the surface morphologies observed in STM images and the electronic structure of the different surface phases observed in high-resolution core-level and valence-band photoemission. @FootnoteText@ @footnote 1@S.C. Erwin and H.H. Weitering, Phys. Rev. Lett. 81, 2296 (1998).

9:40am **SS2-FrM5 STM Study of Metal Row Growth on Si(5 5 12)***, **K.M. Saoud**, I. Samanta, K.M. Jones, A.A. Baski,* Virginia Commonwealth University

The high-index Si(5 5 12)-2x1 surface has recently gained interest as a template for overlayer growth, primarily because of its highly anisotropic row reconstruction. Our recent STM studies have shown that a noble metal such as Ag forms well-ordered overlayer rows on this surface.@footnote 1@ At coverages below 0.25 ML and moderate annealing temperatures (450°C), Ag forms monatomic rows with an inter-row spacing of ~5 nm. These Ag rows nucleate along the more reactive tetramer rows of the surface reconstruction, and are separated by isolated @pi@-chains remaining from the clean surface. At higher temperatures and coverages (>500°C, >0.25 ML), these @pi@-chains are removed and the Ag rows become wider with a strong 3x periodicity. We now have preliminary studies of more reactive metals such as Au and Ca on Si(5 5 12). At moderate annealing temperatures, both metals form overlayer rows that still preferentially nucleate along the tetramers. However, these rows are less well-ordered and are shorter at a given coverage, indicating the enhanced reactivity of these adsorbates. As expected, both metals change their growth behavior at higher annealing temperatures. The Au grows in 3x rows that become substantially more ordered and longer at a given coverage, whereas Ca rearranges the surface into a more complicated undulating row-like structure. In both cases, no remaining structures from the underlying reconstruction are visible. This work clearly demonstrates the utility of the Si(5 5 12) surface as a template for the 1D growth of a variety of metals. @FootnoteText@ @footnote 1@ H.H. Song, K.M. Jones, and A.A. Baski, J. Vac. Sci. Technol. A Jul/Aug 1999.

10:00am **SS2-FrM6 Chemisorption and Dissociation of O@sub 2@ on Pd(111) Studied by STM***, M.K. Rose,* Lawrence Berkeley National Laboratory*; A. Borg,* Norwegian University of Science and Technology, Norway*; F. Besenbacher,* University of Aarhus, Denmark*; D.F. Ogletree, **M. Salmeron**,* Lawrence Berkeley National Laboratory

A variable temperature STM study of chemisorption and dissociation of O@sub 2@ on Pd(111) is presented. Adsorption of O@sub 2@ on Pd(111) at 30K in the submonolayer range causes formation of a superoxo like and peroxo like molecular oxygen species. These two species image differently in STM, the superoxide appears to have weaker corrugation as compared to the peroxide. The superoxide is the more mobile species of the two at 30K. The peroxide display (2x2) structure in ordered areas, which grow in size upon annealing to 100K. Induced by the STM tip, individual O@sub 2@ molecules dissociate into pairs with a preferred separation of 2 lattice spacings, which is the equilibrium spacing in the (2x2)-O structure on Pd(111). Thermal O@sub 2@ dissociation is observed at about 150K. Our data show that the oxygen molecules evaporate from the peroxide island periphery onto the terrace before dissociation. Similar atomic oxygen pair spacings are observed in this case, but the distribution of oxygen on the surface is influenced by subsurface species present in the Pd(111).

10:20am **SS2-FrM7 The Oxidation and Reduction of Pd(111)***, **G. Zheng**, E.I. Altman,* Yale University

Palladium is a promising catalyst for oxidation reactions. Therefore, the oxidation of Pd(111) was characterized using STM, TPD, and LEED. Exposure of Pd(111) to O@sub 2@ resulted in a (2x2) structure, that saturated after exposure to 30 L. To increase the oxygen coverage, NO@sub 2@ was used. Initial exposure of Pd(111) to NO@sub 2@ also produced the (2x2) structure. Further exposure, however, resulted in additional diffraction spots, which persisted until the oxygen coverage reached approximately 1.0 ML. At oxygen coverages between 1.0 - 2.0 ML, a complicated LEED pattern was observed. This pattern could be explained as the superposition of two surface structures, one with a square surface lattice rotated 15° with respect to the Pd(111) substrate, the other with a rectangular surface lattice rotated 30° with respect to the Pd(111) substrate. In STM images, ad-islands and peninsulas were observed in this oxygen coverage regime. The rectangular structure was found on the original Pd(111) terraces, while the square structure was observed on the islands and peninsulas. A Moiré pattern due to lattice mismatch with underlying layers was also observed on the islands and peninsulas. The lattice constant for the square structure was 0.679 nm; and the two lattice constants for the rectangular structure were 0.394 nm and 0.638 nm, respectively, consistent with LEED observations. After further increasing the oxygen coverage, the complicated LEED patterns became faint. At the same time, a low temperature shoulder associated with bulk PdO developed in TPD traces. These results indicate that oxygen can exist in five different states on the Pd(111) surface. The reactivity of these states towards reduction is being characterized by monitoring the rate of disappearance of the different surface oxygen phases by recording STM movies during reduction by CO, H@sub 2@, and CH@sub 3@OH.

10:40am **SS2-FrM8 Experimental and Theoretical STM Imaging of Molecules on Metal Surfaces@footnote 1@**, ***D.N. Futaba,*** University of California, Davis*; C.A. Pearson,* University of Michigan*; A. Loui, S. Chiang, D.M. Jaramillo, D.P. Land,* University of California, Davis

We have imaged the surface structure of benzene coadsorbed with carbon monoxide (CO) on the Pd(111) surface in ultrahigh vacuum using a low temperature (90K) scanning tunneling microscope (STM). In conjunction with low-energy electron diffraction, three distinct overlayer structures have been observed to form as a function of various dosing conditions: two hexagonal structures when predosed with CO, (2@sr@3x2@sr@3)R30° and (3x3), and one rectangular structure. We are currently studying the mechanism by which one hexagonal layer transforms into the other as the benzene coverage increases. Our models of the structure give an overall molecular coverage of 1/3 for both hexagonal structures, suggesting molecular place exchange. We have performed laser induced thermal desorption and thermal desorption spectroscopy measurements to calibrate relative amounts of CO and benzene for the different structures. We also use a simple computational method, based on extended Hückel theory, to calculate STM images expected for the dehydrogenation of cyclohexene to benzene on Pd(111). Based on the proposed bonding geometry by Hunka et al.,@footnote 2@ we expect to see significant differences between the chemisorbed cyclohexene molecules and the resultant benzene molecules. Our calculated images of paraxylene and metaxylene on Rh(111) showed good agreement with existing experimental STM data by Cernota et al.@footnote 3@ Therefore, we expect good agreement between our calculations of orthoxylene on Pd(111) and our experiments in progress. @FootnoteText@ @footnote 1@ Funded by NSF (CHE-95-20366) and CLC Program of Univ. of California. @footnote 2@ D.E. Hunka, T. Picciotto, D.M. Jaramillo, D.P. Land, Surf. Sci., 421, L166 (1999). @footnote 3@ P.D. Cernota, H.A. Yoon, M. Salmeron, G.A. Somorjai, Surf. Sci., 415, 3511 (1998).

11:00am **SS2-FrM9 In-Situ Soft X-ray Studies of Acetylene Oxidation on the Pt(111) Surface**, ***D.J. Burnett,*** *A.M. Gabelnick,* University of Michigan*; D.A. Fischer,* National Institute of Standards and Technology*; J.L. Gland,* University of Michigan

In-situ studies of acetylene oxidation have been performed using Fluorescence Yield Soft X-ray methods for temperatures up to 600 K and pressures up to 0.01 torr. Absolute carbon coverages have been determined in steady-state and dynamic conditions on the Pt(111) surface over an extended pressure and temperature range using in-situ soft X-ray methods. Transient surface concentration measurements were used during these in-situ studies to provide direct measurement of surface reaction rates. Temperature-programmed oxidation of preadsorbed acetylene monolayers (TP-FYNES) on the Pt(111) surface was conducted in oxygen pressures up to 0.01 torr. Acetylene remains on the surface until skeletal oxidation occurs around 350 K, depending on the oxygen pressure. The onset temperature for skeletal oxidation decreased slightly with increasing oxygen pressures. Transient experiments with both acetylene and oxygen in the gas phase were performed over a wide range of pressures and temperatures. Further, detailed mechanistic studies were performed yielding a substantial amount of high quality kinetic rate data. These kinetic studies, coupled with the TP-FYNES results suggest a mechanism limited by C-H bond activation. In addition to the transient studies above, detailed spectroscopy was accomplished via in-situ, soft X-ray fluorescence yield methods to identify the dominant oxidation intermediates. Both acetylene and ethylene oxidation appear to involve the same surface intermediates since both processes are limited by the same rate-determining step. In both instances, oxidation intermediates have been identified and characterized using in-situ fluorescence yield methods.

11:20am **SS2-FrM10 The Adsorption and Decomposition of Trimethylamine on Pt(111)**, *D.-H. Kang,* ***M. Trenary,*** University of Illinois, Chicago

Reflection absorption infrared spectroscopy (RAIRS) and temperature programmed reaction spectroscopy (TPRS) have been used to study the adsorption and decomposition of trimethylamine on Pt(111). In a series of previous RAIRS studies, it was shown that several different molecules containing CN bonds all rearranged on Pt(111) to form the same stable intermediate, aminomethylidyne, CNH@sub 2@. Aminomethylidyne was formed following the initial adsorption of azomethane, methylamine, hydrogen cyanide, and from the hydrogenation of surface CN that was produced from the dissociative adsorption of cyanogen. Furthermore, the hydrogenation of undissociated cyanogen was found to form the H@sub 2@NCCNH@sub 2@ species, which contains the same aminocarbyne functionality as in aminomethylidyne. This suggests that aminocarbynes of the general formula CNRR', where R and R' can be H or an alkyl group, may be common intermediates in surface chemical reactions involving CN-containing molecules. Dimethylaminocarbyne (CN(CH@sub 3@)@sub 2@) is a well-known ligand in the organometallic literature. It could be formed on the Pt(111) surface through the removal of the three H atoms from one of the methyl groups of trimethylamine. The RAIRS and TPRS data obtained so far support the formation of dimethylaminocarbyne as a stable intermediate species formed from the partial dehydrogenation of trimethylamine on Pt(111). A key spectroscopic feature of CN(CH@sub 3@)@sub 2@ is an intense RAIRS band at 1471 cm@super -1@, which is characteristic of the CN stretch in aminocarbynes.

11:40am **SS2-FrM11 Investigation of the Adsorption and Reactions of Thiophene on Sulfided Cu, Mo and Rh Catalysts**, ***M.E. Bussell,*** *P. Mills, D.C. Phillips, B.P. Woodruff, R. Main,* Western Washington University

Infrared (IR) spectroscopy and temperature programmed desorption (TPD) have been used to investigate the adsorption and reactions of thiophene on alumina-supported sulfided Cu, Mo and Rh catalysts over wide ranges of temperature (130-700 K) and pressure (10 @super-9@ - 10 @super3@ Torr). Following adsorption at 130 K, thiophene adsorbs on sulfided Mo and Rh catalysts in an @eta@@super 1@(S) geometry; it has not been possible to determine the adsorption geometry of thiophene on Cu sites of the sulfided Cu catalyst due to low coverage. The coverage of thiophene on sites in the supported metal sulfide particles is observed to increase in the order Cu < Mo < Rh, in agreement with CO chemisorption measurements. Little or no reactivity is observed when the different catalysts are heated in thiophene vapor alone at temperatures up to 700 K. In thiophene/H@sub 2@ mixtures, hydrogenated species are observed to form on sulfided Rh catalysts by 350 K, and by 550 K on sulfided Mo catalysts. Following evacuation to UHV pressures, TPD shows the major products to be butadiene, butenes and butane. The results of these experiments are in good agreement with flow reactor studies of thiophene hydrodesulfurization over these same catalysts.

Surface Science Division
Room 604 - Session SS3+EM-FrM
Reactions on Semiconductors

Moderator: S.F. Bent, Stanford University

8:20am **SS3+EM-FrM1 A Comparative Study of [2+2] Cycloaddition Reactions of Organic Alkenes on Group IV Semiconductor Surfaces**, ***R.J. Hamers,*** *J.S. Hovis, S.C. Coulter,* University of Wisconsin, Madison*; C.M. Greenlief,* University of Missouri, Columbia

Organic alkenes such as cyclopentene can bond to Si(001) and Ge(001) surfaces to produce monolayer organic films that are chemically homogeneous and structurally ordered. The bonding of these molecules to the dimerized Si, Ge, and C (diamond) surfaces 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 surface reactions involves two electrons from the organic alkene and two electrons from the ? orbital of the surface Si=Si, Ge=Ge, or C=C dimers. Solution-phase reactions of organic compounds via [2+2] processes are forbidden by orbital symmetry considerations and are therefore extremely slow. In order to better understand the nature of the analogous surface reactions, we have used infrared spectroscopy, scanning tunneling microscopy, X-ray photoelectron spectroscopy, and quantum chemistry methods to investigate the adsorption of cyclopentene and other simple alkenes on Si and Ge(001) semiconductor surfaces. Our results show that reactions of simple alkenes on Si(001) and Ge(001) surfaces are facile, producing ordered monolayers. Ab initio calculations for Si, Ge, and C clusters indicate that the reactions on Si and Ge surfaces are facile because of the ability of these surface dimers to tilt, facilitating a low-energy, low-symmetry pathway to adsorption on these surfaces. This talk will summarize our recent experimental and computational studies aimed at understanding the nature of cycloaddition reactions of organic alkenes on Group IV semiconductor surfaces. @FootnoteText@ This work was supported in part by the U.S. Office of Naval Research and the National Science Foundation.

8:40am **SS3+EM-FrM2 Novel Organic Monolayer Films on Si(100): Theoretical Studies of Cylocaddition Chemistry**, *J.A. Barriocanal, **D.J. Doren**,* University of Delaware

A class of cycloaddition reactions will be described that can be used to attach monolayer organic films to Si(100). These reactions, known as 1,3-dipolar additions, can be performed with organic molecules containing a wide variety of organic functional groups. Examples include nitro compounds (R-NOO), azides (R-NNN) and their sulfur and phosporous analogs. Density functional theory calculations for prototypical cases show that the molecules chemisorb with negligible activation barrier. As in traditional organic synthesis, having a variety of functional groups that react in a similar way allows some control over the final product by proper choice of the reagent. A complication, in many cases, is that the product of the initial reaction is not the thermodynamic product, and rearrangements will occur. Some guidelines for predicting the most likely rearrangements, based on density functional theory calculations, will be discussed. Potential applications and comparisons to available experimental work will also be described.

9:00am **SS3+EM-FrM3 Formation of Si/Thiophene Hybrid System in UHV by a Hetero Diels-Alder Cycloaddition Surface Synthetic Strategy**, *Y. Cao, **G.Q. Xu**,* National University of Singapore, Singapore

The formation of organic monolayer on semiconductor surfaces has great device applications in biosensors, field effect transistors as templates for the epitaxial layer growth on semiconductors. In this work, the covalent coupling of thiophene monolayer on a semiconductor surface has been attained by a facile way at room temperature in UHV. We demonstrate here a hetero Diels-Alder cycloaddition reaction strategy for chemical modification of a well-defined Si(111)-7x7 surface with thiophene molecules. The concerted [4+2] cycloaddition reaction of thiophene with adjacent rest atom-adatom pair, resulting the formation of a 2,5-dihydrothiophenelike cycloadduct on Si(111)-7x7, has been clearly demonstrated by combined STM and HREELS spectroscopic studies. Documented as the least reactive diene in Deils-Alder cycloaddition reaction due to its high aromaticity, however, the cycloaddition reaction of thiophene on Si(111)-7x7 is facile even under UHV conditions. In addition, the reactivity of thiophene toward the rest atom-adatom pairs on Si(111)-7x7 can be theoretically explained by correlation of the the HOMO and LUMO energy of thiophene molecule and the surface band level for the empty and filled states on Si(111)-7x7. The feasibility of such procedure provides a better understanding of the chemical reactions proceed through semiconductor surfaces, more significantly, offers a potential new methodology for functionalization the semiconductor surfaces with desired control.

9:20am **SS3+EM-FrM4 Kinetics of Abstraction of Monohydride and Dihydride D from Si(100) Surfaces**, *A. Dinger, C. Lutterloh, **J. Küppers**,* Universität Bayreuth, Germany

The interaction of H(D) atoms with Si(100) surfaces and the abstraction of D adsorbed in the monohydride and dihydride phases on Si(100) by H was studied with thermal desorption spectroscopy and direct product rate measurements. H/D atoms were produced in W tube sources heated at 2000 K. H/D atom exposure to clean Si(100) surfaces at 380 K and 640 K lead to the formation of dihydride and monohydride phases with the characteristic desorption peaks at 690 K and 810 K. In addition, after application of high atom fluences, H@sub 2@ (D@sub 2@) peaks were seen at 910 K which are interpreted as a consequence of etching. Etch products were monitored in desorption and during reaction. H atom exposure to monohydride D covered surfaces at 640 K revealed HD and D@sub 2@ as gaseous products. At a saturated monohydride surface about 6% of the adsorbed D occurred in D@sub 2@ products. The kinetics of HD formation is not in accordance with the operation of an Eley-Rideal mechanism. This is most clearly apparent at small D coverages since then the HD rate is constant at decreasing D coverage. Abstraction of D from dihydride phases at 380 K exhibit an Eley-Rideal phenomenology in the HD rates, however a small contribution of D@sub 2@ products (<1%) illustrate that another mechanism also acts in abstraction of D from the dihydride. The results can be explained by the operation of hot-atom mechanisms, in which the probabilities of hot-atom sticking and reaction determine the kinetics of gaseous products formation.

9:40am **SS3+EM-FrM5 The Adsorption and Thermal Decomposition of Dimethylamine Adsorbed on Si(100)**, ***S.M. Casey**, C.P.A. Mulcahy, A.J. Dennis,* University of Nevada, Reno

Dimethylamine (DMA) adsorption on the Si(100)-(2x1) surface has been studied using Auger electron spectroscopy (AES), low-energy electron diffraction, and temperature-programmed reaction spectroscopy (TPRS). It is shown that at room temperature DMA chemisorbs on this surface with a saturation coverage of about 0.5 monolayers. These experiments also show evidence for multilayer formation in this adsorbate system. For doses above the saturation dose level, intact DMA molecules begin to adsorb on top of the surface-bound adsorbate layer. TPRS data show that the decompostion of DMA adsorbed on the Si(100) surface proceeds via two different mechanisms in the monolayer vs. multilayer coverage regimes. The adsorbates directly bound to the surface are shown to decompose via reactions that form gaseous hydrogen and hydrogen cyanide products, while the intact multilayer DMA species decompose to form hydrogen and imine dehydrogenation products. Evidence for formation of both the cyclic ethylenimine species and the straight-chained N-methylmethanimine species in this multilayer regime is presented. Kinetic analysis of the TPRS data shows that the heats of desorption for the two products of the surface-bound adsorbate decomposition (hydrogen and hydrogen cyanide) are much higher than the heats of desorption for the products of multilayer decomposition. AES results show that repeated decomposition of DMA on Si(100) leads to the slow deposition of carbon- and nitrogen-based films, although the thermal deposition efficiency is relatively low and the overall stoichiometry of the resulting films could not be clearly established.

10:00am **SS3+EM-FrM6 Reactivity of Diamond (100) towards Cycloaddition Chemistry**, ***G.T. Wang**, S.F. Bent,* Stanford University*; J.S. Hovis, R.J. Hamers,* University of Wisconsin, Madison*; J.N. Russell, Jr., J.E. Butler,* Naval Research Laboratory*; M.P. D'Evelyn,* General Electric

Diamond has a number of extreme material properties that make it an ideal candidate for a wide range of applications, including electronic devices, electron emitters, multispectral windows, and heat sinks. Similar to Si(100) and Ge(100), the diamond (100) surface undergoes a 2x1 reconstruction in which pairs of atoms are bonded into dimers via a strong sigma bond and a partial pi bond. Recent studies on 2x1 reconstructed Si(100) and Ge(100) have shown that the pi bond of the surface dimers can react with unsaturated hydrocarbons via [2+2] and [4+2] (Diels-Alder) cycloaddition reactions, forming covalently attached ring structures. In this study we investigate the viability of the diamond (100) surface to undergo cycloaddition reactions with cyclopentene and 1,3-butadiene using multiple internal reflection infrared spectroscopy and ab initio quantum chemistry calculations. While cyclopentene can react with the surface only via a [2+2] cycloaddition (which is formally forbidden for concerted reactions by symmetry considerations), 1,3-butadiene can potentially react via a [2+2] or [4+2] cycloaddition due to its conjugated double bond. It was found that both cyclopentene and 1,3-butadiene reacted with the diamond (100) surface at room temperature, although significantly larger exposures of cyclopentene were required. The greater reactivity of 1,3-butadiene versus cyclopentene may be attributable to 1,3-butadiene bonding via a lower-barrier [4+2] pathway not available to cyclopentene. Comparison of cycloaddition reactivity on diamond (100) versus Si(100) and Ge(100) provides insight into the mechanism of these reactions on semiconductor surfaces. These results also demonstrate the viability of organic synthetic routes for modifying the diamond surface.

10:20am **SS3+EM-FrM7 Surface Infrared Spectroscopy of CH@sub x@ Adsorbates during GaAs OMVPE**, ***J.R. Creighton**, K.C. Baucom,* Sandia National Laboratories

We have used surface infrared spectroscopy (SIRS) to identify the adsorbates present on GaAs(001) during organometallic vapor phase epitaxy (OMVPE) and atomic layer epitaxy (ALE). The key advantage of SIRS, as compared to reflectance-difference spectroscopy (RDS) and related UV-vis reflectance techniques, is that the interpretation of infrared spectra is much more straightforward and less ambiguous. One example of the rich spectral information derived with SIRS is seen during the trimethylgallium (TMGa) ALE cycle. During the initial stages of TMGa exposure, methyl groups (CH@sub 3@) bonded to both gallium and arsenic can be detected and differentiated. With time, the methyl-arsenic species disappear and methylene (CH@sub 2@) species (the precursors to carbon incorporation) begin to cover the surface. During low-temperature OMVPE we also detect a significant methyl group coverage, and these results will be compared to the other in-situ optical measurements, e.g. RDS, at similar growth conditions. (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.).

10:40am **SS3+EM-FrM8 Ab initio Study of Adsorption and Decomposition of NH@sub 3@ on Si(100)-(2x1)***, **Y. Widjaja**, M. Mysinger, C. Musgrave,* Stanford University

Deposition of silicon nitride thin films has become a key technology in the microelectronics industry. In silicon nitride deposition, NH@sub 3@ is typically used as the nitriding agent because of its high sticking coefficient and reactivity. In this study, we investigate the atomistic mechanisms for NH@sub 3@ adsorption and initial decomposition on the (2x1) reconstructed Si(100) surface using B3LYP density functional theory (DFT) and by utilizing the cluster model. We present a detailed investigation of the effects of cluster size on the reaction energetics. We find that the Si@sub 9@H@sub 12@ (1-dimer) cluster model does not describe the NH@sub 3@(a) adsorption state well due to the delocalized nature of the electron transfer in forming the NH@sub 3@(a) dative bond. We find that the Si@sub 21@H@sub 20@ (3-dimer) cluster is necessary to fully capture these non-local effects. The 3-dimer model is able to satisfactorily reproduce the results of larger cluster models. We then use the 3-dimer cluster model to study the adsorption and decomposition reactions of NH@sub 3@ on the Si(100)-(2x1) surface. Ammonia is found to adsorb on the down atom of buckled silicon dimers with no activation barrier. This adsorption is exothermic with an adsorption energy of 29 kcal/mol. This adsorption is then followed by dissociation to form NH@sub 2@(a) + H(a) with a low activation energy. Our calculated recombination desorption energy of 51 kcal/mol is found to be in good agreement with the TPD experimental result of 47 kcal/mol. In addition, we also calculate the vibrational spectra of the dissociated species. We find our results to be in good agreement with the experimental HREELS spectra.

11:00am **SS3+EM-FrM9 Reactions of Substituted Aromatic Hydrocarbons with the Si(001) Crystal Surface***, **S.C. Coulter**, J.S. Hovis, M.D. Ellison, R.J. Hamers,* University of Wisconsin, Madison

The surface chemistry of small aromatic molecular systems chemisorbed on the single domain Si(001)-(2x1) face has been investigated using Infrared and X-ray Photoelectron Spectroscopy. Both the [2+2] and the [4+2] Diels-Alder cycloaddition processes are possible. Substitued aromatic hydrocarbons, including toluene, benzonitrile and ortho-, meta- and para-xylene, have been studied to provide clues as to their possible steering effects into a favored bonding geometry. Our data indicates that these reactions are complex and, in some cases, involve multiple bonding configurations. Detailed analysis of the infrared spectra and comparisons with known compounds have been used to help identify the surface products and to provide new understanding of substituent effects during molecular bonding at silicon surfaces.

11:20am **SS3+EM-FrM10 Thermal Hydrogen Reactions with Boron-doped Si(100) Surface***, **B. Gong**,* The University of Texas at Austin*; S.K. Jo,* Kyung Won University, South Korea*; J.G. Ekerdt,* The University of Texas at Austin

The reactions of hydrogen with boron-doped Si(100) have been studied with temperature programmed desorption, high resolution electron energy loss spectroscopy and low energy electron diffraction. Recent studies by our group have illustrated that in the boron concentration range from 0.002 to 0.1 monolayer (ML), SiH@sub 2@ (@beta@@sub 2@) formation is greatly suppressed at 400 K. This inability of the H-passivated Si(100) to undergo the 3x1 reconstruction is associated with the subsurface boron-induced bond strain and silicon dimer vacancy defects. At higher boron coverages (0.2-0.5 ML), H@sub 2@ desorption data show a new, broad desorption peak (@beta@@sub 3@) at ~ 400 K in addition to SiH (@beta@@sub 1@) and SiH@sub 2@ states. The @beta@@sub 1@ and @beta@@sub 2@ desorption energies are unchanged by boron. The new H@sub 2@ desorption peak is related to trihydride formation (SiH@sub 3@) on silicon sites that are associated with second layer boron atoms. Both SiH@sub 3@ and @beta@@sub 3@-H@sub 2@ desorption increase with increasing boron coverage. We propose that the enhanced silicon growth rate found during in situ boron doping is related to the new H@sub 2@ desorption channel that has its origin with SiH@sub 3@ formation. Extensive H-induced surface etching is also seen on intrinsic Si(100) surfaces at 180 K. SiH@sub 4@ desorption at ~600 K has been used as an indicator of H-induced etching, where SiH@sub 3@ forms as a result of H atoms breaking Si-Si back bonds; SiH@sub 2@ formation precedes the formation of the SiH@sub 3@ etch product. This surface etching is sharply reduced on lightly boron-doped Si(100) surfaces, which is in good agreement with the result that low coverage boron prevents SiH@sub 2@ formation on Si(100).

11:40am **SS3+EM-FrM11 Impact of Surface Structure on the Arsine Adsorption Kinetics on GaAs and InP (001)***, **Q. Fu**, L. Li, C. Li, D. Law, R.F. Hicks,* University of California, Los Angeles

Arsine adsorption on the gallium-rich GaAs (001) (4x2) reconstruction and on the indium-rich InP (001) (2x4) reconstruction has been studied by internal-reflection infrared spectroscopy and scanning tunneling microscopy. It was found that AsH@sub 3@ adsorption on the (4x2) follows an autocatalytic mechanism, with the rate proportional to the fraction of occupied and vacant sites. By contrast, AsH@sub 3@ adsorption on the (2x4) follows a Langmuir adsorption mechanism, with the rate depending only on the fraction of vacant sites. We attribute these differences in the reaction kinetics to the impact of the semiconductor surface structure on the adsorption mechanism. The GaAs (4x2) reconstruction is terminated with 3 gallium dimers per unit cell, while the InP (2x4) contains one In-P heterodimer, and 4 In dimers per unit cell. An arsine molecule dissociatively adsorbs onto the group III dimers and transfers hydrogen to a group V dimer site. On the GaAs (4x2), only a few of these latter sites are present, and more are created by adsorption, so the reaction is autocatalytic. Conversely, on the InP (2x4), the latter sites are readily available, and Langmuir adsorption occurs. The decomposition mechanisms of arsine on these surfaces will be discussed in detail at the meeting.

Thin Films Division

Room 615 - Session TF-FrM

In-situ Characterization and Material Process Imaging

Moderator: J.S. Zabinski, Air Force Research Laboratory

8:40am **TF-FrM2 Ion Beam Induced Defects and Phonon Confinement in 2H-WS@sub 2@ by "In-situ/Real-Time" Raman Measurements***, **F.S. Ohuchi**,* University of Washington*; K. Ishioka, M. Kitajima,* National Institute for Metals, Japan

Ion beam bombardment induces chemical and structural changes in the solid surface. This occurs because a large fraction of the incident ion energy goes into bulk processes like atomic mixing, dissociation and reduction, forming defects in the material. Raman scattering is sensitive to small changes that occur in the lattice symmetry of a crystal, thus it has been used as a sensitive structure probe to study the defects in solids. In this paper, we report "in-situ" and "real-time" Raman measurements on tungsten disulfide (WS@sub 2@) single crystals during the bombardment of 5 keV He@super +@ ion beam. Changes in the peak intensity, energy and broadening for the E@sub 2g@ phonon mode were measured as a function of ion dose (1x10@super 12@-4x10@super 16@ ions/cm@super 2@), and the phonon correlation lengths were obtained using "spatial phonon correlation (SPC)" model. The phonon correlation length decreased with ion irradiation dose, and their changes were correlated with our previous investigation on the surface stoichiometry change with ion bombardment (JVST A12(4) 2451, 1994). Appearance of a new shoulder peak at around 416 cm@super -1@ to the A@sub 1g@ peak became evident when the dose exceeded more than 10@super 14@ions/cm@super 2@. This peak is considered as a forbidden mode originated from defect-induced coupling of the longitudinal acoustic (LA) and transverse acoustic (TA) phonons at the K point in the Brillouin zone of the WS@sub 2@ lattice. .

9:00am **TF-FrM3 Toward 'Virtual' Materials Processing Research***, **S.R. LeClair**,* Air Force Research Laboratory **INVITED**

Of the many research challenges in materials science is the development of more comprehensive methods for materials process design and control ranging from bulk materials transformation at the macro scale to increasingly small systems at the nano scale. The unavoidable frontier of the future is 'small-systems', wherein thin-films and MEMs are merely the bow wave to a world of atomic-scale ordering and transitions which will manifest in the interfacial designs of nano-functional building blocks for more portable and efficient systems. Although small-systems have widespread application to Air Force pursuits in becoming a Space Force, the technology will be inevitably driven by the need for more powerful but compact computing and telecommunication devices. Let us assume the inevitability of small-systems, and focus on the more immediate and prerequisite issues relative to materials research and the methods for design, analysis and control of processes to realize small-systems. To enable these methods will require investments - first, in the area of molecular modeling - transforming the various molecular modeling methods from their current use as a limited means of atomic-scale perusal to the simulation of growth processes for the manufacture of small-systems. Also at issue, and potentially more pivotal, is atomic-scale sensing for in situ monitoring of the deposition and self-assembly of nano-functional building blocks and their associated interfaces. We will need in situ, but non-destructive, methods for imaging surfaces and subsurface structures to assess defect densities, electrical, optical and thermal conductivities, size and continuity of granular orientations, etc.

9:40am **TF-FrM5 Stress Evolution during Growth of Epitaxial and Polycrystalline Metal Multilayers***, **V. Ramaswamy**, W.D. Nix, B.M. Clemens,* Stanford University

A complete understanding of the relationship between film stress and microstructure at the various stages of growth and an ability to measure film stress in-situ during growth, provide an opportunity to study film microstructural evolution. In this study, stress evolution during growth of epitaxial and polycrystalline, (111)-oriented Pd/Pt and Pd/Ag multilayers is monitored by in-situ substrate curvature measurement. The initial stress behavior of Pd grown on Ag and Pt is similar in epitaxial and polycrystalline films, with Pd exhibiting a sharp tensile change when grown on Ag and a smaller compressive change followed by a tensile change when grown on Pt. This initial behavior is ascribed to the effects of coherency and surface energy differences between film and underlayer. However, with increasing Pd thickness, remarkable differences are observed in the stress behavior in the epitaxial and polycrystalline samples. In polycrystalline Pd/Pt and Pd/Ag, the tensile stress relaxes with increasing Pd thickness and eventually turns compressive at about 30 Å whereas in the epitaxial samples, the stress in Pd remains tensile even at large thicknesses. The stress behavior of Ag and Pt in Pd/Ag and Pd/Pt multilayers are similar in the epitaxial and polycrystalline cases, with Ag on Pd relaxing completely after the growth of the first monolayer and the development of compressive stress in Pt grown on Pd. The effects of the structural differences between epitaxial and polycrystalline films on the stress behavior are discussed in terms of strengthening mechanisms and susceptibility to the effects of atomic peening.

10:00am **TF-FrM6 Metallic Sputtered Film Evolution Via Real-time/In-situ X-ray Diffraction***, J.F. Whitacre, Z.B. Zhao, B.A. Rainey, **S.M. Yalisove**, J.C. Bilello,* University of Michigan

A laboratory-based in-situ x-ray diffractometer is described. This equipment allows the evolution of sputtered metallic films to be studied during growth. An 18kW rotating anode x-ray source is used in conjunction with an Inel(tm) curvilinear position sensitive detector, which is aligned in the asymmetric or symmetric grazing incidence x-ray scattering (GIXS) geometry. Complete diffraction patterns can be acquired in as little as 2 seconds from films of adequate thickness. The development of texture, stress, grain size, and phase content is observed in coatings consisting of Ta, Cr, and/or CrN. Traditional ex-situ analysis methods are applied to these films after growth and are correlated to the in-situ findings, providing a powerful tool for in-situ process control and optimization. Using this system, films and multilayer coatings can be tailored to have specific microstructural characteristics as they are grown. Data from a number of different experiments will be presented and discussed. This work funded by ARO contracts with numbers DAAH 04-95-1-0120 and 8c DAAG55-98-1-0382.

10:20am **TF-FrM7 In Line Measurement of Ti and TiN Thickness and Optical Constants using Reflectance Data through a Vacuum Chamber Window***, **M.F. Tabet**,* Nanometrics Inc.*; U. Kelkar,* Applied Materials

The thickness and optical constants of titanium and titanium nitride thin films were measured by visible reflectometry through a window of a vacuum deposition system while the wafer is cooling from deposition to room temperature. The measurement system is ultra-compact and was designed for integration into semiconductor processing equipment. This in-line metrology tool does not affect the system throughput. The Ti and TiN films were deposited on 3000 @Ao@ silicon dioxide film on 200 mm silicon wafers using an Applied Materials Endura PVD deposition system. The system was used to measure thin metal films with various thicknesses and deposited using conventional DC magnetron sputtering and Ionized Metal Plasma (IMP) techniques. The optical constants of the Ti and TiN films were modeled through the use of a Lorentz oscillator dispersion model. A standalone production metrology tool was used to measured both ellipsometer and reflectometer data from the same location on the wafer and simultaneously determined the thickness and optical constants model parameters. The dispersion model obtained from the analysis of the combined ellipsometry and reflectometry data was then used to fit the visible reflectance data measured in line. This measurement system can monitor Ti and TiN depositions on every wafer in a production environment.

10:40am **TF-FrM8 Morphology and Growth of Metal Thin Films on Si Probed by In Situ Spectroscopic Ellipsometry@footnote 1@***, **C. Liu**, J. Erdmann, A. Macrander,* Argonne National Laboratory

Here we present results of in situ spectroscopic ellipsometry studies of sputtered thin films of Au, Pt, Pd, Rh, Cr, Cu grown on Si wafers. This study was carried out systematically on incrementally grown metal thin films. Multiple data sets obtained for each film material with incremental thicknesses were analyzed using both flat-film and rough-film models. We found that the initial growth of these metal films on Si is correlated with their chemical bond strength with oxygen in the native oxide of Si. Metals with higher bond strength (such as Cr) grow smoother at the early stage of growth and have a better adhesion to the Si wafer. In metal/Si systems, a Cr thin film is thus commonly added as a "glue" layer between the metal and Si for better adhesion. The Cr film however, becomes rougher as its thickness increases. A glue layer of Cr should not exceed 10 nm to keep the film smooth. Rh films grow smoothly on a thin (6-nm) Cr-covered Si wafer. But on a thick (100-nm) Cr/Si film, they were initially as rough as the thick Cr film. The roughness decreases as the Rh film thickness increases. A relaxation effect was also observed on Rh/Si films. An increase of ~10% in measured Rh thickness was observed two hours after the growth when a flat-film model was used. This puzzle was solved when a rough-film model was applied. The Rh film simply became rougher in vacuum at room temperature and the total mass of Rh did not change. The same Rh film stored in air shrunk to small individual droplets 6 months later. These findings are important in our x-ray mirror applications. @FootnoteText@ This work is supported by the U.S. Department of Energy, BES, under contract no. W-31-109-ENG-38

11:00am **TF-FrM9 Stabilization of High Deposition Rate Reactive Magnetron Sputtering of Oxides by In-Situ Spectroscopic Ellipsometry and Plasma Diagnostics***, **M. Vergöhl**, N. Malkomes, B. Hunsche, B. Szyszka, T. Matthée,* Fraunhofer Institute for Surface Engineering and Thin Films, Germany

High deposition rates are of essential importance in reactive magnetron sputtering on architectural glass. To reach high deposition rates and a high transparency of oxide films with constant properties during the full target lifetime, it is required that the process can be stabilized in a specific window within the transition mode. In general, the control of the plasma parameters alone (i.e. partial pressure, optical emission intensity, plasma impedance) is not sufficient for the definition of an operating point with constant film parameters. Therefore, a control system is proposed that is based on a combination of a short-term stabilization of the plasma and a long-term stabilization employing an in-situ spectroscopic ellipsometer. For niobium and titanium oxide, both an optical emission monitor and reactive gas partial pressure measurement were employed. In addition, it turns out that the specific deposition rate, i.e. deposition rate divided by the power density, is a suitable control parameter. Compared to the oxide mode, the deposition rate of Nb2O5 and TiO2 films deposited in the transition mode could be enlarged by a factor of 3-4. The films were grown at different process parameters (oxygen partial pressure, target power, absolute pressure, mid-frequency and DC-technique) onto unheated substrates. Nearby in-situ ellipsometry, ex-situ spectroscopic ellipsometry at different angles of incidence was applied to study the optical properties and the morphology of the films.

11:20am **TF-FrM10 In-situ Structural, Chemical and Electrical Characterization of WO@sub 3@ Sensor Films***, **S.A. Ding**, C.S. Kim, R.J. Lad,* University of Maine, U.S.

Tungsten trioxide thin films are useful as active elements in semiconducting metal oxide conductance-type gas sensors. To explore the correlation between deposition parameters/post-deposition processing and sensing characteristics of the films, we have used a multi-chambered UHV system to deposit WO@sub 3@ films on r-cut sapphire. In-situ chemical and electrical characterizations of the films were then carried out before and after the exposure to target gases such as H@sub 2@S, Cl@sub 2@ and DMMP. The films were grown using rf magnetron sputtering of a W target in O@sub 2@/Ar mixtures ranging from 0 to 80% O@sub 2@. Additional deposition parameters included growth temperature, rf power and total pressure. Both in-situ RHEED and ex-situ XRD data indicate that a variety of film structures including amorphous, polycrystalline and highly textured films can be achieved by varying those parameters. In-situ conductivity measurements acquired using a four-point van der Pauw method show that the stoichiometry and microstructure have an influence on the electrical behavior of the sensor films. One other important parameter in dictating the electrical characteristics of the sensor films is found to be the deposition rate, which is altered by varying the rf power, O@sub 2@/Ar ratio and the total pressure. The conductivity measurements indicate that the higher rate yields higher baseline conductivity. In-situ XPS study of the films shows the formation of stable surface species upon exposure to the target gases. The observed chemical modification of the surface is discussed within the context of a dependence of sensor behavior on the post-deposition processing of the films.

11:40am **TF-FrM11 Growth and In Situ Characterization of Thin Films by a Dual-Plasma System**, ***E.C. Samano***, *G. Soto, R. Machorro,* CCMC-UNAM, Mexico

Thin films of CN@sub x@, SiO@sub x@Nsub y@ have a tremendous potential to be used in the mechanical and optical industry due to its unique mechanical and dielectric properties, respectively. The stoichiometric control of these films is highly important to manage their desired properties. A dual-plasma system has been set up to provide free radicals from a solid target by laser ablation, and atoms and ions in gas phase by an ECR source. These highly reactive species are deposited on a single crystal silicon substrate. The stoichiometry and properties of carbon nitride and silicon oxynitride films are studied as a function of N@sub 2@ and O@sub 2@ gas pressure, respectively, and the several PLD and ECR deposition parameters. The films are in situ analyzed in an adjacent analysis chamber by AES, XPS and EELS to determine the chemical stability and bonding of their compounds.

Vacuum Technology Division
Room 610 - Session VT-FrM

Vacuum Systems, Design, and Engineering

Moderator: L.A. Smart, Brookhaven National Laboratory

8:20am **VT-FrM1 Electron-Cloud-Induced Effects in the APS Storage Ring***, ***R.A. Rosenberg***, *K.C. Harkay,* Argonne National Laboratory

Synchrotron radiation interacting with the vacuum chamber walls in a storage ring produces photoelectrons that can be accelerated by the beam and scatter from the walls, producing secondary electrons. If the secondary-electron yield (SEY) coefficient of the wall material is greater than one, the electron intensity can be amplified (termed "multipactoring") and a runaway condition can develop. This "electron cloud" can degrade the stored beam through direct interaction or by electron-stimulated desorption of gases from the chamber walls. The energy and intensity of the electron cloud is strongly dependent on both the amount of charge in each bunch of the stored beam and their temporal distribution. In order to obtain direct evidence of the properties of the electron cloud, a special aluminum (SEY > 1) vacuum chamber was built and inserted into the Advanced Photon Source (APS) storage ring. The chamber contains ten rudimentary electron-energy analyzers. Measurements to date have shown that the intensity and electron energy distribution are highly dependent on the temporal spacing between adjacent positron bunches and the amount of current contained in each bunch. Dramatic increases in pressure are observed when the temporal distribution and intensity of the bunches are configured to maximize multipactoring. Results of measurements of the electron energy distribution and concurrent pressure will be presented and discussed in terms of models of the electron cloud. *The submitted manuscript has been created by the University of Chicago as Operator of Argonne National Laboratory ("Argonne") under Contract No. W-31-109-ENG-38 with the U.S. Department of Energy. The U.S. Government retains for itself, and others acting on its behalf, a paid-up, nonexclusive, irrevocable worldwide license in said article to reproduce, prepare derivative works, distribute copies to the public, and perform publicly and display publicly, by or on behalf of the Government.

8:40am **VT-FrM2 Vacuum Simulation of Linac Components to Optimize Pump Designs***, ***L.S. Tung***, Lawrence Livermore National Laboratory, US; *P. Shoaff, S. Shen,* Lawrence Livermore National Laboratory

Methods have been developed to model the pressure history in linear accelerator components using Mathematica@footnote 1@ and Mathcad.@footnote 2@ The components are divided into sub-volumes represented as a lumped volume at a point in space. These sub-volumes are separated by conductances. The pressure distribution is obtained by solving the gas load equations for each sub-volume simultaneously for each time during pumpdown to the base pressure. Our models include the pressure dependence of speeds for all the system pumps as determined by a numerical fit to graphs provided by the vendor. Also included is the time-dependent outgassing history of oven-brazed copper based on recent rf cavity experiments and textbook data. Additionally, cryogenic pumping effects have been integrated into the modeling of the vacuum response in a superconducting linac structure. With these models, we can optimize the manifold design and pumping configurations. Our approach is especially useful for extrapolating costs for a large-scale linac. @FootnoteText@ *Work performed under the auspices of the U. S. Department of Energy by the Lawrence Livermore National Laboratory under contract number W-7405-ENG-48. @footnote 1@Mathematica software by Wolfram. @footnote 2@Mathcad software by Math Soft.

9:00am **VT-FrM3 Experiences on the Preparation and Assembly of The Superconducting Linear Accelerator for the TESLA Test Facility**, ***A. Matheisen,*** TESLA Collaboration, DESY, Germany **INVITED**

A description of the superconducting TESLA Test Facility Linear Accelerator, which is under installation at DESY by the TESLA collaboration and of the planed VUV FEL user facility will be given. We report on the infrastructure and technologies for preparation of accelerator components. Detailed information on the preparation sequences for cavities and the connected UHV beam-line equipment under cleanroom conditions of class 10 ASTM quality will be given. Experiences in handling, preparation and the efforts in quality control of components with the need of minimum contamination by particulates to reach acceleration gradients of above 25 MV/m will presented. @FootnoteText@ *TESLA Collaboration: Armenia: Yerevan Pysics Institue, P.R.China: IHEP Beijing, Tsinghua Univ. Beijing, Finland: Inst. of Physics Helsinki, France: CEA/DSM Saclay, IN2P3 Orsay, Germany: May Born Inst. Berlin, DESY Hamburg/ Zeuthen, Univ. Wuppertal, Univers. Hamburg, Univ. Frankfurt, GKSS Geesthacht, FZ Karlsruhe, TU Darmstadt, TU Berlin, TU Dresden, RWTH Aachen, Univ. Rostock. Italy: INFN Frascati, INFN Legnaro, INFN Milano, INFN Roma II, Poland: Polish Acad. of science, Univ. Warsaw, INP Cracow, Univ. of Mining &Metallurgy, polish Atomic Energy Agency Energy Agency, Soltan Inst. for Nuclear Studies, Russia: JINR Dubna, IHEP Portvino, INP Novosibirsk, INR Troitsk, USA Argonne National Lab. Cornell Univ., FNAL, UCLA

9:40am **VT-FrM5 APT LEDA CCDTL "HOT MODEL" Vacuum System**, ***T.J. Whelan***, AlliedSignal Federal Manufacturing and Technologies; *P.O. Leslie,* Los Alamos National Laboratory

The vacuum system for the APT/LEDA/CCDTL (Accelerator Production of Tritium/ Low Energy Demonstration Accelerator/Coupled-Cavity Drift Tube Linac) Hot Model has been installed and is currently operating at Los Alamos National Laboratory (LANL). The Hot Model has been built to test a new concept in accelerator technology. The vacuum system was designed and partially assembled and then shipped to LANL for final assembly and installation on the APT/LEDA/CCDTL. The system was designed for both flexibility and low cost. Simple outgassing and conduction models were used to predict pumping needs. This design contains almost no custom parts, which allows for quick and inexpensive changes as needed. The system consists of three pumping stages: roughing, turbomolecular, and ion and utilizes all four of the available ports on the Hot Model. This has allowed the system to reach a better level of vacuum than the originally anticipated need. @FootnoteText@ Work performed at AlliedSignal FM&T which is Operated for the United States Department of Energy under Contract No. DE-ACO4-76-DP00613.

10:00am **VT-FrM6 DA@PHI@NE Vacuum System**, ***A. Clozza***, *V. Chimenti, C. Vaccarezza,* Istituto Nazionale di Fisica Nucleare, Italy

A 510 MeV high luminosity @PHI@-factory is operating at INFN Fascati National Laboratory, Italy. The accelerator complex consists of a full energy Linac, a small damping ring and a double electron-positron high current storage ring. We describe in the following the main rings vacuum system. The design is based on the requirement of 1x10@super -9@ mbar as dynamic pressure with a gas load of about 1x10@super -4@ mbar l/s per ring. The main features of the vacuum system are: all metal aluminum vacuum chamber with proper surface finishing; special alloy bolt set; monolithic water cooled copper synchrotron light absorbers; high capacity titanium sublimation pumps; lumped and distributed sputter ion pumps and high capacity non evaporable getter pumps.

10:20am **VT-FrM7 Thin-walled Vacuum Chambers of Austenitic Stainless Steel*, B.C. Moore,*** Consultant

It is proposed, and recommended, that vacuum chambers and systems to be built of austenitic stainless steel should be designed for the thinnest walls possible, consistent with structural integrity under atmospheric pressure. The reason for this design goal is to greatly reduce the time, effort and cost needed to outgas the chambers to reach the desired and specified vacuum level. Of course, this is directly contrary to the universally accepted concern with permeation of atmospheric hydrogen. This concern has recently been shown to be greatly exaggerated. Atmospheric permeation is at least 100 times less than previously estimated, and is possibly non-existent. Errors in the previous estimate will be briefly summarized. Published outgassing of two relatively thin-walled chambers will be discussed. Methods to predict the hydrogen outgassing rates for specific wall thicknesses and bakeout procedure will be given. Vacuum oven bakes result in a flat, uniform atomic hydrogen concentration profile within the wall and give clean, unoxidized surfaces; the instantaneous outgassing rate is directly proportional to the hydrogen recombination coefficient (at the bake temperature), and to the hydrogen concentration level, while the time required for this rate to decay varies linearly with the wall thickness. In contrast, an 'in situ' bake, with atmosphere on one side and vacuum on the opposite side of the wall, results in an asymmetric concentration profile, with a minimum on the atmospheric side and a maximum on the vacuum side. To further confuse the issue, room temperature operation also causes an asymmetric concentration profile, but in the opposite direction, with the minimum on the vacuum side. Thin walls can be stiffened with rolled in ribs which are substantially thicker than the wall itself. This ribbed structure can be further strengthened by coaxial wraps over the ribs, or by longitudinal bars added outside the ribs. Methods of measuring and calibrating the hydrogen outgassing rates, and of presenting the data, will be discussed briefly.

10:40am **VT-FrM8 Increased Utilization of Semiconductor Process Equipment through Comprehensive Downstream By-product Management*, T.E. Nilsson,*** Nor-Cal Products, Inc.

Fab maintenance personnel and equipment manufacturers share the common goal of extending preventative maintenance intervals and reducing wafer defects in process equipment in order to increase return on investment. Condensable by-product accumulation in forelines, dry pumps and exhaust lines is a significant contributor to wafer defects and planned and unplanned maintenance. Vacuum components, such as heater jackets and foreline traps, can extend preventative maintenance intervals dramatically when applied properly to a specific process. A Comprehensive Downstream Solution is one that first takes into account the specific process chemistries, temperatures and pressures, as well as any equipment constraints. The array of vacuum components and special treatments are passed through two filters: component configuration and a cost of ownership model. Component configuration considers the effect on the performance of the components by changing their relative position in the system. A cost of ownership model is developed with the customer for each option proposed showing the cost of the improvement and the pay back in terms of savings on maintenance and increased production.

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